

## 5.0 Application of Chemical Reaction Codes

### 5.1. Background

Determination of species distributions for dissolved major and trace constituents, including radionuclides, is necessary to understand the processes that control the chemistry of soil-water systems. Several processes will control the thermodynamic activities of dissolved species and, to some extent, their mobility in surface and ground waters and bioavailability to man. These processes are described in detail in Chapter 2 and references cited therein. The processes include the following:

- Aqueous complexation
- Oxidation/reduction
- Adsorption/desorption
- Mineral precipitation/dissolution

The distribution of aqueous species in a multi-component chemical system, such as those in soil-water environments, can only be reliably calculated from a combination of accurate analyses of water compositions and a competent chemical reaction model. Computerized chemical reaction models based on thermodynamic principles may be used to calculate these processes depending on the capabilities of the computer code and the availability of thermodynamic and/or adsorption data for aqueous and mineral constituents of interest. Use of thermodynamic principles to calculate geochemical equilibria in soil-water systems is well established and described in detail in many reference books, such as Bolt and Bruggenwert (1978), Garrels and Christ (1965), Langmuir (1997), Lindsay (1979), Morel (1983), Nordstrom and Munoz (1985), Sposito (1989, 1994), Stumm and Morgan (1981), and others. The reader is referred to these sources for detailed discussions and examples of specific applications relative to the thermodynamic principles and equations that govern these calculations.

Because of the great importance of the aqueous speciation, adsorption, and solubility processes relative to the concentrations and mobility of contaminants that may leach from waste, an understanding of the capabilities and application of chemical reaction models is essential. This understanding is additionally important because these models are used for both the scientific and legal aspects of risk and performance assessment studies of waste disposal and mitigation of environmental contamination.

The purpose of this chapter is to provide a brief conceptual overview of chemical reaction codes and their use in addressing technical defensibility issues associated with data from  $K_d$  studies. Particular attention is given to the capabilities of EPA's MINTEQA2 code, including the types of conceptual models the code contains to quantify adsorption. Issues pertaining to the availability of databases for these adsorption models and the status of the MINTEQA2 aqueous speciation and solubility database for radionuclides are also discussed.

### 5.1.1 Definition of Chemical Reaction Modeling

Chemical reaction models/codes are referred to by several terms in the literature. The term may include either of the adjectives “chemical” or “geochemical,” often depending on the technical field of expertise of the author and/or anticipated audience. Additionally, the models/codes can be referred to as reaction, equilibrium, speciation, or mass transfer<sup>1</sup> (and others) models/codes, although some of these terms refer to submodel capabilities. Throughout this report, the terms “chemical reaction models” and “chemical reaction codes” will be used as collective terms for all variations of these models and codes.

A chemical reaction model is defined here as the integration of mathematical expressions describing theoretical concepts and thermodynamic relationships on which the aqueous speciation, oxidation/reduction, precipitation/dissolution, and adsorption/desorption calculations are based. A chemical reaction code refers to the translation of a chemical reaction model into a sequence of statements in a particular computer language. We define a competent chemical reaction model as a model that contains all the necessary submodels and important aqueous complexes, solids and gases for the important elements of interest required to adequately interpret a given data set.

Most chemical reaction models are based on equilibrium conditions, and contain limited or no kinetic equations in any of their submodels. Some processes, such as aqueous speciation and cation or anion exchange, are closely approximated by equilibrium conditions over short time frames of hours to days. On the other hand, kinetic factors may limit other processes, such as some precipitation/dissolution and redox-sensitive reactions, from reaching equilibrium over reaction periods of tens of years or more. Moreover, without information or assumptions regarding the rate of release of the contaminant of interest from its source term, such as contaminated soils or a decommissioning site, modeling calculations cannot provide an estimate of the total mass (*i.e.*, mass present in aqueous solution plus associated mineral phases) of a contaminant released in the environment under review. At best, chemical modeling based on equilibrium conditions may provide estimates of bounding limits for some processes depending on the reactions being considered. Because of the limited availability of kinetic data and incorporation of kinetic algorithms into chemical reaction codes, this is an important area for future experimental studies and development of chemical reaction models. Readers are referred to references on reviews of chemical reaction models cited later in this chapter for more details on this issue.

Because thermodynamic data typically do not have the resolution to distinguish among different isotopic forms of contaminant-containing aqueous species or solids, geochemical modeling

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<sup>1</sup> *Mass transfer* is the transfer of mass between 2 or more phases that includes an aqueous solution, such as the mass change resulting from the precipitation of a mineral or adsorption of a metal on a mineral surface. In contrast, *mass transport* is the time-dependent movement of one or more solutes during fluid flow.

calculations do not provide any information on the distribution of the different contaminant isotopes present in the aqueous, gaseous, or associated solid phases. However, in most situations, radionuclide isotopes will react the same as natural (stable) isotopes of the element. By assuming ideal isotopic mixing or exchange, one can estimate the distribution of any selected isotopes among the bulk elemental distribution.

### ***5.1.2 Reviews of Chemical Reaction Models***

Numerous reviews of chemical reaction codes have been published. Some of the more extensive reviews include those by Jenne (1981), Kincaid *et al.* (1984), Mercer *et al.* (1981), Nordstrom *et al.* (1979), Nordstrom and Ball (1984), Nordstrom and Munoz (1985), Potter (1979), and others. These reviews have been briefly described in Serne *et al.* (1990). The reviews discuss issues such as:

- Basic mathematical and thermodynamic approaches that are required to formulate the problem of solving geochemical equilibria in aqueous solutions
- Applications for which these codes have been developed and used, such as the modeling of adsorption equilibria, complexation and solubility of trace metals, equilibria in brine solutions and high-temperature geothermal fluids, mass transfer, fluid flow and mass transport, and redox balance of aqueous solutions
- Selection of thermodynamic data and development of thermodynamic databases
- Limitations of chemical reaction codes, such as the testing of the equilibrium assumption, application of these models to high-ionic strength aqueous solutions (*e.g.*, the ion association versus ion interaction conceptual models), the reliability of thermodynamic databases, and the use of validation to identify inadequacies in the conceptual models developed with chemical codes.

Table 5.1 provides a sampling of some chemical reaction codes that have been described in the literature and mentioned in published proceedings, such as Erdal (1985), Jackson and Bourcier (1986), Jacobs and Whatley (1985), Jenne (1979), Loeppert *et al.* (1995), Melchior and Bassett (1990), and the reviews cited above. The reader is directed to these published proceedings and reviews for the appropriate reference to the documentation of each code. Although this list of chemical reaction models is not meant to be complete and continues to expand each year, it demonstrates the diversity of codes that exist, and, in some cases, the evolution of some codes.

**Table 5.1.** Chemical reaction models described in the literature.

ADSORP	EQUIL	MINTEQ	SOILCHEM
AION	EQUILIB	MINTEQA1	SOLGASWATE
ALCHEMI	EVAPOR	MINTEQA2	R
AQ/SALT	FASTCALC	MIRE	SOLMNEQ
ASAME	FASTPATH	MIX2	SOLMNEQ.88
BALANCE	GEOCHEM	NOPAIR	SOLVEQ
C-Salt	GEOCHEM-PC	PATH	SYSTAB
CHEMIST	GIBBS	PATHCALC	THERMAL
CHEMTRN	GMIN	PATHI	WATCH1
CHES	HALTAFALL	PHREEQE	WATCHEM
COMICS	HARPHRQ	PHRQPITZ	WATEQ
DISSOL	HITEQ	REDEQL	WATEQ2
ECES	HYDRAQL	REDEQL.EPAK	WATEQ3
ECHEM	IONPAIR	REDEQL2	WATEQ4F
EHMSYS	KATKHE	RIVEQL	WATEQF
EQ3	KATKLE1	SEAWAT	WATEQFC
EQ3NR	MICROQL	SENECA	WATSPEC
EQ6	MINEQL	SENECA2	
EQBRAT	MINEQL2	SIAS	

Nordstrom and Ball (1984) discuss the issue of why so many chemical reaction codes exist. They attribute this diversity of codes to (1) the lack of availability, (2) inadequate documentation, (3) difficulty of use of some chemical codes, and (4) the wide variety of calculational requirements that include aqueous speciation, solubility, and/or adsorption calculations for aqueous systems that range from simple, chemical systems associated with laboratory experiments to complex, multi-component systems associated with natural environments. No single code can do all of the desired calculations in a perfectly general way. Typically the more general and comprehensive a geochemical code is, the more difficult and costly it is to use. Another factor may be that scientists are inherently reluctant to use any computer code that they and their immediate coworkers have not written.

### *5.1.3 Speciation-Solubility Versus Reaction Path Codes*

Jenne (1981) divides chemical reaction codes into 2 general categories: aqueous speciation-solubility codes and reaction path codes. All of the aqueous speciation-solubility codes may be

used to calculate aqueous speciation/complexation,<sup>1</sup> and the degree of saturation (*i.e.*, saturation index) of the speciated composition of the aqueous solution with respect to the solids in the code's thermodynamic database. Some aqueous speciation-solubility codes also include the capabilities to calculate mass transfer between a single initial and final state, that results from mineral precipitation/dissolution and/or adsorption/desorption reactions. Chemical reaction codes, such as WATEQ, REDEQL, GEOCHEM, MINEQL, MINTEQ, and their later versions, are examples of codes of this type.

Reaction path codes include the capabilities to calculate aqueous speciation and the degree of saturation of aqueous solutions, but also permit the simulation of mass transfer due to mineral precipitation/dissolution or adsorption onto adsorbents as a function of reaction progress. Typical applications include the modeling of chemical changes associated with the interaction of a mineral assemblage and ground water (*e.g.*, INTERA, 1983, and Delany, 1985) or the release of radionuclides from a proposed glass waste form (*e.g.*, Bourcier, 1990) as a function of time. Computationally, 1 unit of reaction progress means that 1 unit of gaseous or solid reactant (*e.g.*, radioactive waste source term) has reacted with an aqueous solution in contact with solid phases with which the solution is already in equilibrium. At each step of reaction progress, the code calculates the changes or path of mineral and gaseous solubility equilibria that are constraining the composition of the aqueous solution, the masses of minerals precipitated and/or dissolved to attain equilibrium, and the resulting composition of the aqueous solution. Examples of reaction path codes include the PHREEQE, PATHCALC, and the EQ3/EQ6 series of codes.

#### ***5.1.4 Adsorption Models in Chemical Reaction Codes***

Various adsorption models have been incorporated into a small number of chemical reaction codes to calculate the mass of a dissolved component adsorbing on a user-specified mineral phase, such as iron hydroxide that coat mineral grains in soil. The adsorption modeling capabilities in these codes have been briefly reviewed by others (*e.g.*, Goldberg, 1995, and Davis and Kent, 1990) and will not be duplicated here. The options vary from code to code. Adsorption models incorporated into chemical reaction codes include non-electrostatic, empirical models as well as the more mechanistic and data intensive, electrostatic, surface complexation models. Examples of non-electrostatic models include the partition (or distribution) coefficient ( $K_d$ ), Langmuir isotherm, Freundlich isotherm, and ion exchange models. The electrostatic, surface complexation models (SCMs) incorporated into chemical reaction codes include the diffuse layer model (DLM)

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<sup>1</sup> *Complexation* (*i.e.*, complex formation) is any combination of dissolved cations with molecules or anions containing free pairs of electrons. *Species* refers to actual form in which a dissolved molecule or ion is present in solution. Definitions are taken from Stumm and Morgan (1981).

A list of acronyms, abbreviations, symbols, and notation is given in Appendix A. A list of definitions is given in Appendix B

[or diffuse double layer model (DDLDM)], constant capacitance model (CCM), Basic Stern model, and triple layer model (TLM).

Some of the chemical reaction codes identified in the reviews by Goldberg (1995) and Davis and Kent (1990) as having adsorption models include HARPHRE (Brown *et al.*, 1991), HYDRAQL (Papelis *et al.*, 1988), SOILCHEM (Sposito and Coves, 1988), and the MINTEQA series of chemical reaction codes, including MINTEQA2 (Allison *et al.*, 1991) developed for the U.S. Environmental Protection Agency (EPA). Compared to other codes, MINTEQA2 contains some of the most extensive options for modeling adsorption, including all of the models listed above, except for the Basic Stern model. The MINTEQA2 adsorption model options are discussed further in Section 5.2, and their associated equation and reaction formulations as coded within MINTEQA2 are described in Section 5.3. It should be noted that the partition coefficient ( $K_d$ ), Langmuir, and Freundlich models incorporated into MINTEQA2 are formulated in terms of species activities,<sup>1</sup> and not the more traditional approach of total concentrations of dissolved metal. This variation in modeling approach and the rationale for its use are discussed in Section 5.2.

Some of these models are briefly described in Chapter 2. The reader is also referred to reference texts by Langmuir (1997), Morel (1983), Sposito (1984), and Stumm and Morgan (1981) for more detailed background descriptions, associated equations and data needs, and model comparisons pertaining to these adsorption models.

As noted in Chapter 2, the electrostatic, surface complexation models, although robust, are not expected to have a significant impact on contaminant transport and risk assessment modeling due to their significant data needs and more complex equation formulations. Detailed descriptions, comparisons, and derivations of the relevant equations and reactions associated with these models are described in Westall and Hohl (1980), Morel *et al.* (1981), Barrow and Bowden (1987), Davis and Kent (1990), and others. The data needs and associated derivation (*i.e.*, parameterization) of model constants are discussed by Morel *et al.* (1981), Turner (1991), and Goldberg (1995). The electrostatic models were developed to provide a mechanistic description of adsorption reactions in systems containing a pure single phase of an amorphous or crystalline metal oxide. Numerous studies have demonstrated their success in predicting adsorption of trace metals in such simplified systems (*e.g.*, Turner, 1993). Application of such adsorption models to natural systems where the reactive surfaces include a combination of impure phases, clays, and humic materials are limited. The adsorption behavior of such systems unfortunately cannot be modeled assuming that the

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<sup>1</sup> In general terms, the *activity* of an ion is its effective concentration that determines its behavior to other ions with which it might react. The activity of an ion is equal to its concentration only in infinitely dilute solutions, and is related to its analytical concentration by an activity coefficient,  $\gamma$ . Activities, activity coefficients, and associated thermodynamic relationships are discussed in detail in texts such as Glasstone (1972), Lewis and Randall (1961), Morel (1983), Sposito (1984), and Stumm and Morgan (1981).

adsorptive properties of a phase mixture, such as soil, can be readily predicted by adding the adsorption constants for the individual solid phases in some normalized fashion.

Numerous papers have been published relative to the application of non-electrostatic and electrostatic adsorption models to modeling the migration of radionuclides released from high (HLW) and low level (LLW) radioactive waste disposal facilities. These include reviews and references cited therein by Serne and Muller (1987) and Turner (1993,1995) for application to HLW disposal and Serne *et al.* (1990) for application to LLW disposal issues. The reader should also be aware of an extensive literature review by Berry (1992a,b,c) of adsorption studies conducted in the United Kingdom and the international community on sorption relative to the release and transport of radionuclides in the near<sup>1</sup> and far field. The literature review is published as 3 reports. The first report summarizes studies funded by the United Kingdom (UK) Nirex and Department of the Environment (UK DoE). The second report contains an extensive bibliography, including reference citations and complete abstracts, of United Kingdom and international publications on the subject area. The third report compares the objectives and approaches used in studies funded by Nirex and UK DoE to those in related studies undertaken by the international community.

### ***5.1.5 Output from Chemical Reaction Modeling***

The results from chemical reaction codes vary depending on the capabilities, design of the output report, and user-selected options for each code. The output may be in the form of a report directed to a printer, and/or a total or partial report stored as an ASCII (American Standard Code for Information Interchange)-formatted file for future use in word processing or spreadsheet software or as input for other scientific application software. The output can be extensive depending on the options used for the modeling calculations and the level of output report requested by the user.

The output report from MINTEQA2 chemical reaction code (Allison *et al.*, 1991) will be used as a typical example. The MINTEQA2 code was developed by EPA and is described in greater detail in Section 5.2. For each modeling calculation, the output can include the following:

- Documentation and constraints applied to the calculation
  - Name of the data file and the date and time of modeling calculations
  - Documentation to describe modeling calculation
  - Listing of the model parameters used to control the calculations (*e.g.*, maximum number of permitted iterations, method for calculating activity coefficients, alkalinity option, units used for input of water composition, temperature), level of output report (*e.g.*, short versus long report), and type of selected adsorption algorithm

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<sup>1</sup> The “near field” is that portion of a contaminant plume that is near the point source and whose chemical composition is significantly different from that of the uncontaminated portion of the aquifer. The “far field” refers to that which is not the “near field.”

- Listing of the input water composition
  - Listing of any controls (*e.g.*, pH, Eh, redox equilibria) applied to the calculation
  - Listing of any additions or modifications made as part of the input file to the code's thermodynamic database
  - Listing of any adsorption reactions and associated constants used for adsorption reaction calculations
  - Listing of any solid phases and associated masses considered for mass transfer calculations
  - Listing of any gases whose solubility will control the concentration of a dissolved constituent (*e.g.*, solubility of CO<sub>2</sub> gas to fix the total concentration of dissolved carbonate)
- Results of aqueous speciation calculations
    - Number of iterations required for the aqueous speciation calculation to converge
    - Calculated concentrations, activities, activity coefficients, equilibrium constants as modified for ionic strength and temperature for each aqueous species extracted from the code's thermodynamic database and included in the calculation
    - Charge imbalance before and after calculation of aqueous speciation
    - Listing of the distribution of important (*i.e.*, greater than 1 percent of the total concentration of a dissolved component) uncomplexed and complexed aqueous species for each valence form of each dissolved component (See "Glossary" for technical definition of "component.")
  - Results of solubility calculations
    - Degree of saturation of the starting water composition relative to equilibrium solubility of every solid in the code's thermodynamic database containing the components included in that water analysis
    - Listing of the reaction stoichiometries and associated temperature-corrected equilibrium constants for each solid phase included in the calculation
  - Results of mass transfer calculations at each stage of calculations where a solubility and/or adsorption equilibrium condition is reached
    - Repeat of all speciation results for new calculated water composition
    - Repeat of the solubility results for new calculated water composition
    - Calculated mass of each element in dissolved, precipitated, and/or adsorbed states for new calculated water composition

Parts of example output reports from MINTEQ are listed and explained in detail in Allison *et al.* (1991) and Peterson *et al.* (1987a).

### 5.1.6 Assumptions and Data Needs

Chemical reaction models may be used to predict the concentrations of elements, such as uranium, that may be present in an aqueous solution. This type of modeling calculation requires the user to select either a solubility or an adsorption reaction to constrain the maximum concentration limit of a contaminant or any other dissolved constituent. The modeling process is based on the following assumptions and data needs for the environment of interest:

- For a solution-concentration limit based on a solubility reaction, the mineral phase selected as the solubility control for the contaminant of interest must have known thermodynamic data (*e.g.*, solubility constant). The selection of the solid phase must be technically defensible in that the phase is known to exist in analogous aqueous environments and have rates of precipitation and dissolution that are not limited by kinetics.
- For a solution-concentration limit based on an adsorption reaction,<sup>1</sup> the substrate (*e.g.*, an iron-oxyhydroxide coating) selected as the adsorption control for the contaminant of interest must be technically defensible relative to the soil or sediment being modeled. The adsorption parameters must be known for the contaminant of interest and its major competing ions for the substrate and the range of appropriate environmental conditions.
- The reactions or conditions that control the pH, redox conditions, and concentrations of complexing ligands (*e.g.*, dissolved carbonate) for the derived aqueous solution must be assumed and technically defensible.
- The model must have an adequate thermodynamic database that includes all the necessary aqueous species, redox reactions, minerals, and sorption substrates for the contaminant of interest and for the other constituents of environmental importance.
- The composition of water (in particular, pH, Eh, and alkalinity) contacting the contaminant-containing phases must be known.
- Most chemical modeling calculations will be limited to equilibrium conditions, because of the general absence of kinetic rate values for the aqueous speciation, solubility, and/or sorption reactions involving the contaminant of interest and other constituents of environmental importance. Equilibrium (actually steady state) conditions are likely in the far field, but are less likely in the near-field environment or at the boundaries of contaminant plumes.

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<sup>1</sup> When using the partition coefficient ( $K_d$ ) or Freundlich adsorption models, the predicted solution-concentration limits are only valid when modeling trace concentrations of a contaminant of interest.

### 5.1.7 Symposiums on Chemical Reaction Modeling

Both the diversity and interdependency of research efforts associated with chemical reaction modeling are effectively demonstrated by the papers presented at several symposiums held on this subject. Some of these conferences are listed in Table 5.2.

The symposiums typically include papers on a range of subjects, such as theoretical advancements; model and code development, including documentation; application studies of equilibrium and mass transfer codes, transport and coupled codes, and surface processes; database development, including thermodynamic data, kinetic data, and data on organic compounds; modeling sensitivities; and model validation.<sup>1</sup>

The reader is encouraged to peruse these proceedings. The proceedings' papers show that the development of chemical reaction models is concurrent with the expansion and improvement of thermodynamic databases for aqueous species and solids and for adsorption, as well as with application studies that test the validity of these models and their associated databases.

**Table 5.2.** Examples of technical symposiums held on development, applications, and data needs for chemical reaction modeling.

Published Proceedings	Date of Symposium	Location	Sponsorship
Jenne (1979)	Sept. 11-13, 1978	Miami Beach, Florida	Amer. Chem. Soc.
Erdal (1985)	June 20-22, 1984	Los Alamos, New Mexico	U.S. Department of Energy (DOE) and U.S. Nuclear Regulatory Commission (NRC)
Jacobs and Whatley (1985)	Oct. 2-5, 1984	Oak Ridge, Tennessee	NRC
Jackson and Bourcier (1986)	Sept. 14-17, 1986	Fallen Leaf Lake, California	DOE and LLNL
Melchior and Bassett (1990)	Sept. 25-30, 1988	Los Angeles, California	Amer. Chem. Soc.
Loeppert <i>et al.</i> (1995)	Oct. 23-24, 1990	San Antonio, Texas	Soil Sci. Soc. Amer. and Amer. Soc. Agron.

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<sup>1</sup> *Model validation* is the integrated test of the accuracy with which a geochemical model and its thermodynamic database simulate actual chemical processes. In contrast, *code verification* is the test of the accuracy with which the subroutines of the computer code perform the numerical calculations.

## 5.2 MINTEQA2 Chemical Reaction Code

### 5.2.1 Background

The MINTEQA2 computer code and its predecessor versions are described by Allison *et al.* (1991, MINTEQA2), Brown and Allison (1987, MINTEQA1), Peterson *et al.* (1987a, MINTEQ), and Felmy *et al.* (1984, MINTEQ). The MINTEQ code was developed with EPA funding. It was originally constructed by combining the mathematical structure of the MINEQL code (Westall *et al.*, 1976) with the thermodynamic database and geochemical attributes of the WATEQ3 code (Ball *et al.*, 1981a).

The MINTEQA2 code is used in conjunction with a thermodynamic database to calculate complex chemical equilibria among aqueous species, gases, and solids, and between dissolved and adsorbed states. Conceptually, the code can be considered as having the following 4 submodels: (1) aqueous speciation, (2) solubility, (3) precipitation/dissolution, and (4) adsorption. These submodels include calculations of aqueous speciation/complexation, oxidation-reduction, gas-phase equilibria, solubility and saturation state (*i.e.*, saturation index), precipitation/dissolution of solid phases, and adsorption. The MINTEQA2 code incorporates a Newton-Raphson iteration scheme to solve the set of mass-action and mass-balance expressions.

The reader is referred to the references and user guides listed above for details regarding the use of the MINTEQ code, types and examples of geochemical equilibria calculations possible with this code, the basic equations on which the model is based, and examples of input and output files.

### 5.2.2 Code Availability

MINTEQA2 (Version 3.11) is the most current version of MINTEQ available from EPA. It is compiled to execute on a personal computer (PC) using the MS-DOS computer operating system. The MINTEQA2 software package distributed by EPA also includes PRODEFA2, which is an user-interactive code used to create and modify input files for MINTEQA2.<sup>1</sup> The user is referred to the description of PRODEFA2 in Allison *et al.* (1991).

Copies of the files containing the source and executable codes for MINTEQA2 and PRODEFA2, thermodynamic databases, example input data sets, and documentation are available by mail from

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<sup>1</sup> Versions of MINTEQ modified to operate on DOS and Macintosh personal computer systems are also available from commercial sources.

Center for Exposure Assessment Modeling (CEAM)  
U.S. Environmental Protection Agency  
Office of Research and Development  
Environmental Research Laboratory  
960 College Station Road  
Athens, Georgia 30605-2720

These files may also be downloaded using the Internet by accessing CEAM's home page. The address of the CEAM home page is

*[ftp://ftp.epa.gov/epa\\_ceam/wwwhtml/ceamhome.htm](ftp://ftp.epa.gov/epa_ceam/wwwhtml/ceamhome.htm)*

The MINTEQA2 code and documentation are located under "software products" in "...CEAM *software products* and related *descriptive information* is..." The CEAM home page may also be accessed via EPA's home page at

*<http://www.epa.gov>*

by selecting "software" in "EPA Data Systems and Software," and then "Center for Exposure Assessment Modeling."

Training courses are commonly held on the use of chemical reaction modeling techniques and the application of the MINTEQA2 code. In the past, MINTEQ training has been provided to EPA and NRC by their supporting national laboratory and private contractors. Allison Geoscience Consultants, Inc.<sup>1</sup> have, for example, conducted several MINTEQA2 modeling workshops. The Pacific Northwest National Laboratory (Peterson *et al.*, 1987a) has provided MINTEQA2 training to the NRC. Short course announcements from the Environmental Education Enterprises, Inc. (E<sup>3</sup>)<sup>2</sup> for environmental science and engineering training also included MINTEQ workshops.

### **5.2.3 Aqueous Speciation Submodel**

The MINTEQA2 code can be considered as having the following 4 parts: (1) an aqueous speciation submodel, (2) solubility submodel, (3) precipitation/dissolution submodel, and

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<sup>1</sup> The use of commercial business and product names is for descriptive purposes only, and does not imply endorsement by EPA or PNNL.

Allison Geoscience Consultants, Inc., 3920 Perry Lane, Flowery Branch, Georgia 30542.

<sup>2</sup> Environmental Education Enterprises, Inc. (E<sup>3</sup>), 2764 Sawbury Boulevard, Columbus, Ohio 43235-4580.

(4) adsorption submodel. The aqueous speciation submodel is fundamental to all other submodels. It first uses the MINTEQA2 thermodynamic database to calculate the activities of the uncomplexed and complexed aqueous species for an initial water composition. The activities of individual aqueous species are corrected for ionic strength using the Davies or extended Debye-Hückel equations.

The aqueous speciation of a dissolved contaminant can only be determined using thermodynamic calculations such as those formulated in the aqueous speciation submodel of chemical reaction codes. Except for pH, which is the negative of the logarithm of the activity of the uncomplexed  $H^+$  aqueous ion, the user typically supplies the total concentrations of a chemical constituent in an input file for a chemical reaction code. Most common analytical techniques measure the total concentrations of a dissolved constituent such as uranium, and not the concentration of any of its many individual species such as  $UO_2^{2+}$ ,  $UO_2OH^+$ ,  $UO_2(CO_3)_2^{2-}$ ,  $UO_2SO_4^-(aq)$ , or  $UO_2PO_4^-$ .

Aqueous speciation, and hence the testing of solubility hypotheses in the solubility submodel, is only reliable if the quality of the chemical analysis of the water is adequate. The description of the water composition is usually obtained by direct measurement of major cations and anions, pH, Eh, and trace constituents. As a quality check of the water chemical analysis, the MINTEQA2 code calculates the cation/anion balance for each speciated water composition. The cation/anion balance is calculated using the equation

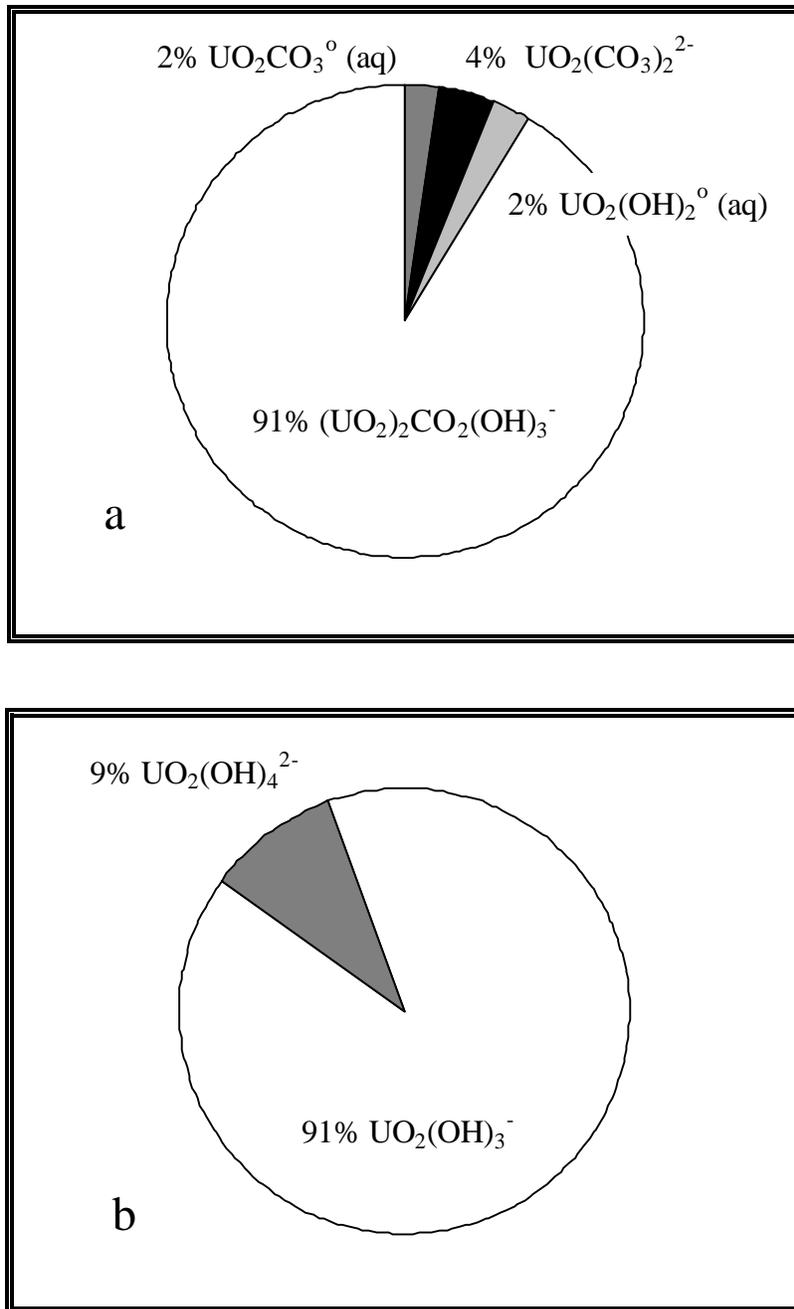
$$\text{Cation/Anion Balance(\%)} = \frac{[\text{Anions (equiv./l)} - \text{Cations (equiv./l)}]}{[\text{Anions (equiv./l)} + \text{Cations (equiv./l)}]} \times 100. \quad (5.1)$$

For simple groundwater compositions and accurate analytical work, the cation/anion balance should not exceed a few percent (Hem, 1985).

The importance of complexation is discussed in Chapter 2 and elsewhere, such as Langmuir (1997), Lindsay (1979), Morel (1983), and Stumm and Morgan (1981). Complexation of dissolved metals with ligands, such as carbonate, will increase the total concentration of a dissolved metal in a soil-water system, and affect its availability for sorption and migration in geochemical systems. The output from the MINTEQA2 aqueous speciation submodel identifies, based on the data in the code's thermodynamic database, the distribution (*i.e.*, dissolved masses) of uncomplexed and complexed aqueous species for the constituents included in the input water composition.

#### 5.2.3.1 Example of Modeling Study

Krupka and Serne (1998) used the MINTEQA2 code to analyze solubility limits for contaminants that may be released from a hypothetical low-level radioactive waste (LLW) disposal facility being considered in a NRC performance assessment test case analysis. The species distributions plotted for dissolved U(VI) in Figure 5.1 were taken from the MINTEQA2 calculations by Krupka and Serne. They provide a good example of the type of information



**Figure 5.1.** Distribution of dominant U(VI) aqueous species for leachates buffered at pH 7.0 by local ground water (Figure 5.1a) and at pH 12.5 by cement pore fluids (Figure 5.1b). [Adapted from MINTEQA2 modeling results of Krupka and Serne (1998).]

provided by the aqueous speciation submodel. Figure 5.1a shows the distribution of dominant species (*i.e.*, greater than 1 percent of total dissolved mass) of dissolved U(VI), respectively, for leachates buffered at pH 7.0 by the local ground water. This distribution can be contrasted to that in Figure 5.1b which shows the distribution of dominant U(VI) species at pH 12.5 by pore fluids derived from ground-water interactions with cementitious materials in the hypothetical LLW disposal facility. At pH 7.0, the speciation of dissolved U(VI) is dominated by uranyl carbonate complexes. At very basic pH conditions, the anionic uranyl hydrolysis species dominate the chemistry of dissolved U(VI). The speciation results clearly demonstrate that major differences can occur in the speciation of a dissolved metal as a function of different solution chemistries, such as pH.

#### 5.2.3.2 Application to Evaluation of $K_d$ Values

As noted in Chapter 2 and published references, such as Morel (1983), Sposito (1989, 1994), Stumm and Morgan (1981), and others, the ionic nature and composition of the dominant aqueous species for a contaminant are important factors relative to its adsorption behavior on reactive mineral surfaces. Moreover, as demonstrated in the example given above, the ionic nature and composition of the dominant aqueous species are dependent on the composition, pH, and redox conditions of a surface or ground water.

If thermodynamic data exist for the important aqueous species of a contaminant of interest, chemical reaction models *provide the most cost and time effective means of predicting the dominant aqueous species* that could exist for practically any water composition. The rate at which these calculations can be done is limited only by the rate at which a user can enter the input data, given the fast speeds of processors used in modern personal computers. The user can rapidly evaluate whether the dominant species is(are) cationic or anionic, as well as how their compositions might be affected by complexation with dissolved ligands such as carbonate and phosphate. If there is uncertainty relative to the pH evolution or ligand content of a water, the user may then quickly modify the input value(s) and complete a series of sensitivity analyses to determine how the ionic charges and compositions of the dominant aqueous species change.

This information can then be used to substantiate the conceptual model that is being used for adsorption for a particular contaminant. For example, if 90 percent of the mass of a dissolved contaminant is present in anionic form, is this consistent with low or high  $K_d$  values that one might find reported in the literature? If the calculations indicate strong complexation with dissolved sulfate, are the default  $K_d$  values in transport or risk assessment models, such as MEPAS, conservative estimates relative to this specific site chemistry? If toxicology studies indicate that an uncomplexed species, such as  $\text{Cu}^{2+}$ , is the important actor relative to bioavailability, how does this affect the predicted risk when the aqueous speciation calculations indicate that 99 percent of the mass of dissolved copper is present as a carbonate complex in a given water? Chemical reaction models provide an effective tool for calculating the responses in aqueous speciation to different conceptual models that one might consider for soil-water systems.

For example, Kaplan *et al.* (1998) conducted laboratory batch  $K_d$  experiments to study the effects of background geochemistry on the sorption of U(VI) on natural sediments. The MINTEQA2 code was used to calculate the aqueous speciation of U(VI) in a groundwater before and after equilibrium with sediments. The modeling results indicated dissolved U(VI) was present as essentially all aqueous anionic U(VI)-carbonate complexes [*e.g.*,  $\text{UO}_2(\text{CO}_3)_3^{4-}$ ] at high pH conditions. Studies by Waite *et al.* (1994) and others have shown that these complexes, due to their anionic nature, tend to sorb appreciably less to sediments than cationic U(VI) complexes which are present at lower pH conditions.

#### 5.2.4 Solubility Submodel

After calculating the aqueous speciation for a given water composition, solubility-equilibria hypotheses are tested. Ion activity products (IAP) are calculated from the activities of the component (or basis) species,<sup>1</sup> using the stoichiometries of the solubility reactions for minerals and other solids in the thermodynamic database. These activity products are then compared to the equilibrium constants ( $K_{r,T}$ )<sup>2</sup> stored in the database for the solubilities for the same solids, to test the assumption that certain of the dissolved constituents in the aqueous solution are in equilibrium with particular solid phases. Saturation indices,  $[\log (\text{IAP}/K_{r,T})]$ , are calculated to determine if the water is at

$$\text{Equilibrium:} \quad \text{Log} (\text{IAP}/K_{r,T}) \approx 0 , \quad (5.2)$$

$$\text{Oversaturated:} \quad \text{Log} (\text{IAP}/K_{r,T}) > 0 , \quad (5.3)$$

or

$$\text{Undersaturated:} \quad \text{Log} (\text{IAP}/K_{r,T}) < 0 , \quad (5.4)$$

with respect to a specified solid phase. This information allows one to ascertain permissible equilibrium solubility controls for dissolved constituents in that water. This water may be a surface or ground water, or a laboratory solution used for solubility or  $K_d$  measurements.

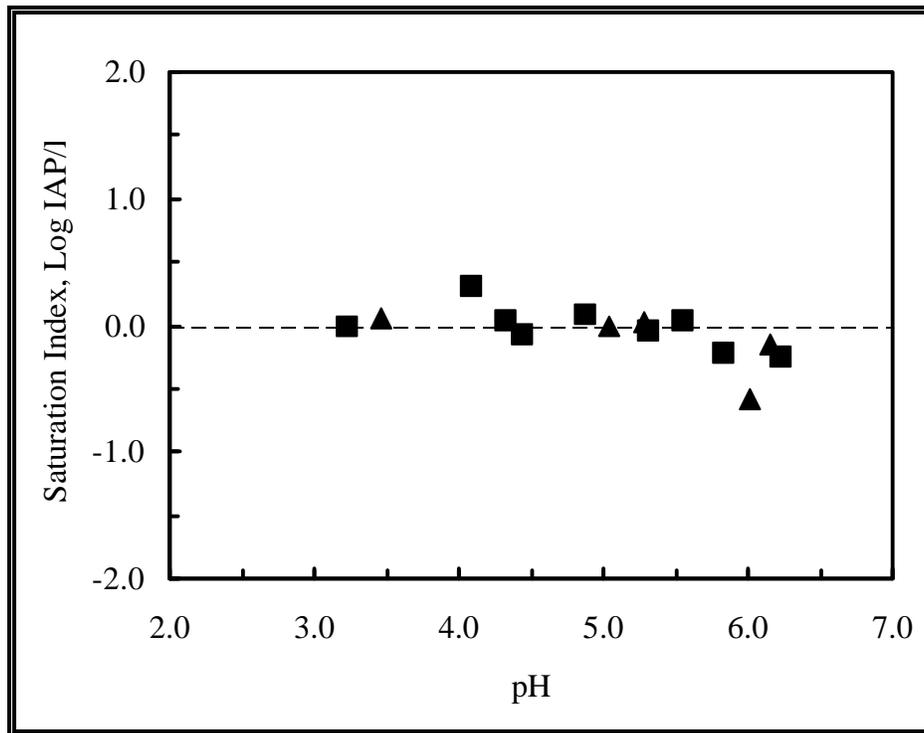
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<sup>1</sup> Component (or basis) species are the “basis entities or building blocks from which all species in the system can be built” (Allison *et al.*, 1991). Examples include  $\text{Mg}^{2+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{CO}_3^{2-}$ , and  $\text{SO}_4^{2-}$  for magnesium, hexavalent uranium [U(VI)], inorganic carbon, and oxidized sulfur [S(VI)], respectively. The set of components in MINTEQA2 is predefined. They are a set of linearly independent aqueous species in terms of which all aqueous speciation, redox, mineral, and gaseous solubility reactions in the MINTEQA2 thermodynamic database are written.

<sup>2</sup> Mineral solubility reactions in the MINTEQA2 database are written as formation (*i.e.*, precipitation) reactions. The solubility product,  $K_{sp,T}$ , (see Chapter 2), which is a commonly used term in the literature, refers to the equilibrium constant,  $K_{r,T}$ , for a mineral solubility reaction written as a dissolution reaction.

#### 5.2.4.1 Example of Modeling Study

Figure 5.2 shows the saturation indices calculated by Krupka *et al.* (1983)<sup>1</sup> for the mineral rutherfordine ( $\text{UO}_2\text{CO}_3$ ) for published analyses of solution samples taken from laboratory uranium solubility studies. The saturation index results demonstrate that these solution samples calculate to be at or very near equilibrium with respect to rutherfordine based on the available thermodynamic data for this mineral and U(VI) aqueous species included in the modeling calculations. Rutherfordine may have therefore precipitated during the course of the solubility studies reported in the cited literature.



**Figure 5.2.** Saturation Indices calculated for rutherfordine ( $\text{UO}_2\text{CO}_3$ ) as a function of pH for solution analyses from Sergeyeva *et al.* (1972). [Adapted from WATEQ4 modeling results of Krupka *et al.* (1983). The filled square and triangle symbols refer, respectively, to solutions analyses from 25 and 50°C experiments by Sergeyeva *et al.* (1972)]

<sup>1</sup> Although Krupka *et al.* (1983) used the WATEQ4 chemical reaction code, their results are analogous to the types of saturation index calculations permitted with the MINTEQ2A code.

#### 5.2.4.2 Application to Evaluation of $K_d$ Values

Chemical reaction codes can be used to analyze the adequacy of laboratory measurements of  $K_d$  values for a particular soil-water system. As noted in Chapter 3, solubility limits have sometimes been exceeded during the process of making laboratory measurements of  $K_d$  values. This can result when the concentration of the contaminant spike introduced to the equilibration vessel is too great and/or when the initial chemical conditions, such as pH, vary greatly during the course of the measurements.

By modeling the aqueous speciation and saturation indices for the initial and final compositions of aqueous solutions present in the  $K_d$  experiments, the user can test if any solubility limits were exceeded during the measurements. In those cases where a contaminant-containing solid is precipitated, the determined  $K_d$  values are measurements of both solubility and adsorption processes and will result in an over-prediction of contaminant attenuation (via only adsorption processes) in the soil-water system.

Kaplan *et al.* (1998) conducted laboratory batch  $K_d$  experiments to study the effects of background geochemistry on the sorption of U(VI) on natural sediments. MINTEQA2 calculations indicated that dissolved U(VI) was present as essentially all aqueous anionic U(VI)-carbonate complexes. Waite *et al.* (1994) and others have shown that these complexes, due to their anionic nature, tend to sorb appreciably less to sediments than cationic U(VI) complexes present at lower pH values. However, the  $K_d$  values measured by Kaplan *et al.* (1998) increased from 1.07 to 2.22 ml/g as the pH increased from 8.17 to 9.31, and were >400 ml/g at  $\text{pH} \geq 10.3$ . Kaplan *et al.* (1998) used MINTEQA2 saturation index calculations to show that the apparent increase in U(VI)  $K_d$  values was due to the precipitation of uranium-containing solids and not to U(VI) adsorption to the sediment.

#### 5.2.5 Precipitation/Dissolution Submodel

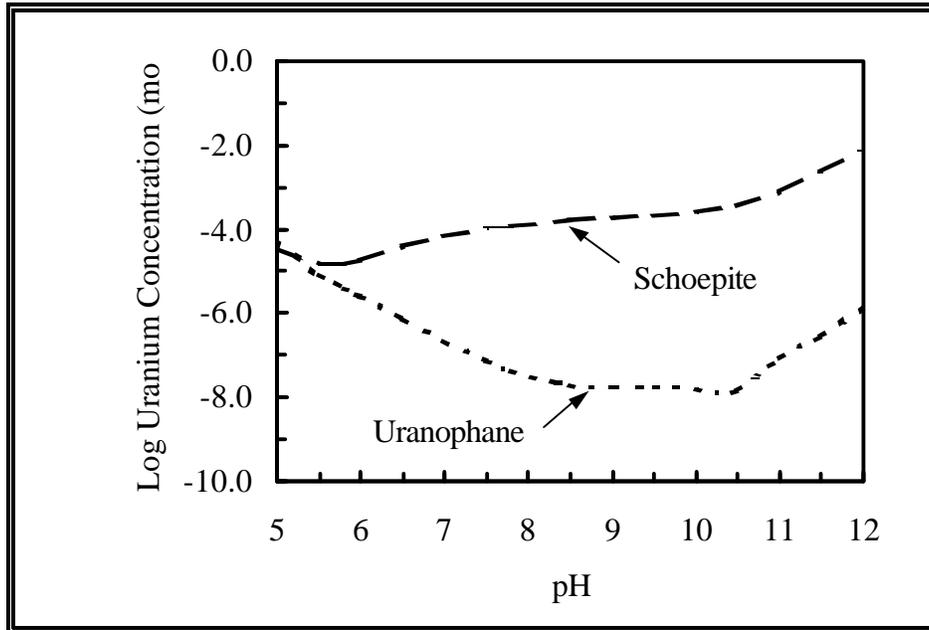
The results from the solubility model are in turn used by the MINTEQA2 as input for the precipitation/dissolution submodel. Application of this submodel is optional. The user may select this submodel and its different options to predict the mass of a solid phase(s) that precipitates or dissolves in the modeled system. The mass transfer submodel determines the mass of a solid phase(s) (*e.g.*, a contaminant-containing solid or a mineral present in a soil) that precipitates from a ground water or dissolves from a soil-water system. If a given water composition calculates to be oversaturated, [ $\log(\text{IAP}/K_{r,T}) > 0$ ], with respect to a solid phase(s) considered in the modeling problem, the mass transfer model will decrease (*i.e.*, precipitate a solid phase) the masses of the appropriate dissolved constituents until the water composition is at equilibrium, [ $\log(\text{IAP}/K_{r,T}) = 0$ ], with respect to that solid phase(s). The MINTEQA2 output lists the mass of solid precipitated per a set volume of the system being modeled. If a given water composition calculates to be undersaturated, [ $\log(\text{IAP}/K_{r,T}) < 0$ ], with respect to a solid phase(s) selected in the modeling problem, the mass transfer model will increase (*i.e.*, dissolve a solid phase) the

masses of the appropriate dissolved constituents until the water composition is at equilibrium with respect to that solid phase(s) or until the user-specified finite mass of that solid has been completely dissolved. For those solids originally designated as having finite masses, the MINTEQA2 output gives the masses per set system volume of any of these solids remaining at final equilibrium.

#### *5.2.5.1 Example of Modeling Study*

The solubility limits calculated by Krupka and Serne (1998) demonstrate one of several applications for a precipitation/dissolution submodel. Maximum concentration limits for dissolved americium, neptunium, nickel, plutonium, radium, strontium, thorium, and uranium were calculated using MINTEQA2 for 2 ground-water environments associated with a hypothetical LLW disposal system. The 2 limiting environments included: (1) a cement buffered system, wherein the leachate pH is controlled at values above 10 by the effective buffering capacity of the concrete, and (2) a ground-water buffered system, wherein the leachate pH and related solution parameters are dominated by the local ground-water system.

Figure 5.3 shows the maximum concentrations calculated by Krupka and Serne (1998) for total dissolved uranium as a function of pH. The predicted concentration limits are based on the equilibrium solubilities of schoepite [ $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ ] and uranophane [ $\text{Ca}(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{SiO}_4)_2 \cdot 3\text{H}_2\text{O}$ ]. These 2 solids were selected based on published phase-stability information and knowledge of the geochemistry of contaminant aqueous systems. Schoepite precipitates readily in short-duration laboratory experiments conducted at ambient temperatures. Because the concentration of dissolved uranium in equilibrium with schoepite is higher than the solubilities of other uranium solids that precipitate under these conditions or in nature, concentration limits based on schoepite are therefore expected to be highly conservative. The presence of alkali and/or alkaline earth ions at high pH conditions results in the precipitation of alkali/alkaline earth uranyl compounds that control the solubility of uranium at concentrations lower than those resulting from equilibrium with schoepite. Therefore, the solubility of uranophane may provide a more realistic solubility limit for dissolved uranium, especially at high pH conditions. Uranophane is known to exist in uranium-loaded cementitious mixtures and thus may be a realistic solubility control for dissolved uranium in cement dominated systems.



**Figure 5.3.** Maximum concentration limits calculated for total dissolved uranium as a function of pH based on the equilibrium solubilities of schoepite and uranophane.

#### 5.2.5.2 Application to Evaluation of $K_d$ Values

Chemical reaction codes can be used to calculate bounding, technically-defensible maximum concentration limits for dissolved contaminants as a function of key composition parameters (e.g., pH) of any specified soil-water system. The concentration of a dissolved contaminant predicted with default or site specific  $K_d$  values used in transport or risk assessment models may exceed the concentration limit based on solubility relationships. In these instances, the solubility-limited concentration may provide a more realistic bounding value than one based on a  $K_d$  value for the assessment calculation, and could have an important impact on the estimated level of risk. If a calculated concentration limit is based on the solubility of a mineral that is known to precipitate under analogous chemical conditions and over reasonable time frames, then the user knows that the dissolved concentrations of this contaminant in an actual, open soil-water system cannot exceed these values and will most likely be significantly less than these values due to adsorption and/or coprecipitation processes.

Moreover, as with the aqueous speciation calculations discussed in Section 5.2.3, mass transfer calculations can be rapidly and inexpensively repeated using a chemical reaction code to determine

their sensitivity to a wide range of chemical parameters for a soil-water systems. This includes easily measured parameters, such as pH, and analytical values that might have a wide range of uncertainty, such as the concentration of a dissolved complexant.

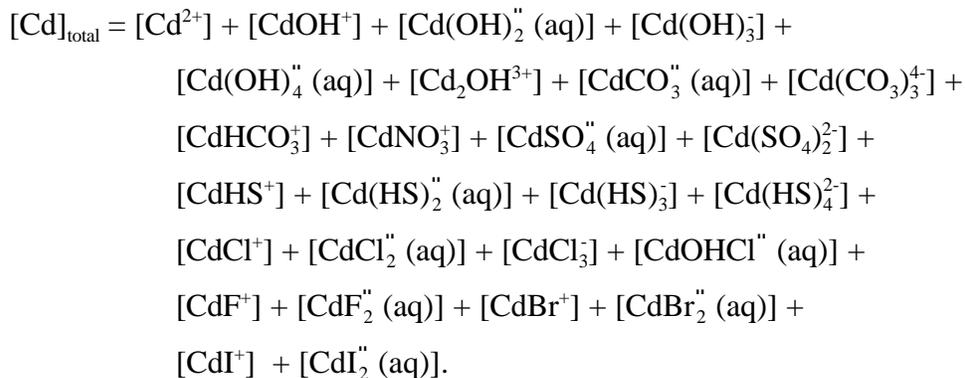
### 5.2.6 Adsorption Submodel

The MINTEQA2 also includes a submodel to calculate the adsorption of dissolved constituents onto the surfaces of solid phases that can be selected by the code user. The MINTEQA2 code includes 7 adsorption model options. These are:

- Non-electrostatic adsorption models
  - Activity partition coefficient ( $K_d^{\text{act}}$ ) model
  - Activity Langmuir model
  - Activity Freundlich model
  - Ion exchange model
- Electrostatic adsorption models
  - Constant capacitance model (CCM)
  - Diffuse layer model (DLM)
  - Triple layer models (TLM).

The equations and reactions that support these models, as coded in MINTEQA2, are described in greater detail in Section 3. These descriptions and associated equations are adapted from Allison *et al.* (1991).

The  $K_d^{\text{act}}$ , Langmuir, and Freundlich models in MINTEQA2 are formulated in terms of species activities, and not the more traditional approach of total concentrations of dissolved metal. In the latter case, the total concentrations of a dissolved metal M would equal the sum of the concentrations of all of its dissolved complexed and uncomplexed species. For example, using the species listed in the MINTEQA2 thermodynamic database, the total concentrations of dissolved cadmium,  $[\text{Cd}]_{\text{total}}$ , in the absence of any organic complexants in the water, could include the following species:



In the presence of organic complexants,  $[Cd]_{total}$  could also include, in addition to the cadmium species listed above, the concentrations of aqueous cadmium complexes containing citrate, acetate, EDTA, HEDTA, or other organic complexes.

A total concentration approach would therefore assume that all species of metal M adsorb with equal strength. Experimental data suggest, however, that only certain aqueous species react with the surfaces of a mineral [*e.g.*, Waite *et al.* (1994)]. Based on this assumption, these non-electrostatic models have been reformulated, as those coded in MINTEQA2, in terms of the activities of adsorbing species to provide activity-based models. The purpose of this approach is to reduce the dependency of the model parameters to effects from ionic strength and aqueous complexation of the adsorbing metal by effectively allowing the adsorption of only selected aqueous species of each metal.

Limitations remain, however, regarding these activity formulations of the  $K_d^{act}$ , Langmuir, and Freundlich models which restricts their range of applicability. These non-electrostatic adsorption models do not consider: charge balance on surface sites and adsorbed species, electrostatic forces between the adsorbing species and charge surface of the mineral, and reactions between the mineral and dissolved constituents other than the adsorbing metal. The effect of these processes changes with variations in the composition of an aqueous solution. These processes are, however, incorporated into the more robust, but more data intensive, electrostatic “surface complexation” adsorption model options in MINTEQA2.

The MINTEQA2 code includes the reaction components and formalisms necessary to enter the required adsorption data for any of the adsorption models. The code does not however have an adsorption database for these models. The user must provide the set of surface reactions and the associated equilibrium constants as part of the input data set. MINTEQA2 requires that this information be supplied relative to the adsorption of constituents onto specific mineral phases, such as amorphous ferric hydroxide  $[Fe(OH)_3 (am)]$ , and not a multi-mineral phase material, such as a soil or crushed rock. Examples of MINTEQA2 input files that include the adsorption modeling option are included in the data files distributed by EPA, and are also listed in Allison *et al.* (1991 Appendix D) and Peterson *et al.* (1987a). These examples demonstrate the major data requirements for some of the adsorption model options in MINTEQA2.

#### 5.2.6.1 Examples of Modeling Studies

Modeling studies by Peterson *et al.* (1986), Davis and Runnells (1987), Loux *et al.* (1989), and Turner *et al.* (1993) are examples of the use of MINTEQ adsorption model options. Peterson *et al.* (1986) and Davis and Runnells (1987) studied ground-water contamination associated with waste impoundments for uranium mill tailings using laboratory and computer modeling techniques. Peterson *et al.* (1986) modeled the adsorption of arsenic, chromium, lead, selenium, and zinc using the triple layer model (TLM) in MINTEQ. Their conceptual model was based on the assumption that adsorption of these metals occurred only on amorphous ferric hydroxide  $[Fe(OH)_3 (am)]$  that precipitated and dissolved during the course of their experiments.

Adsorption parameters for the TLM for amorphous ferric hydroxide were taken from published sources. The results of the adsorption calculations were in good agreement with some results from their laboratory experiments.

Davis and Runnels (1987) used MINTEQ to successfully model the behavior of zinc observed in laboratory column experiments. They assumed that the concentration of dissolved zinc measured in their solution samples was controlled by adsorption on amorphous ferric hydroxide [Fe(OH)<sub>3</sub> (am)] that precipitated as a result of pH changes occurring in their experiments. The adsorption of zinc on Fe(OH)<sub>3</sub> (am) was calculated using the TLM in MINTEQ. Davis and Runnels describe the selection of adsorption parameters used for the TLM.

Loux *et al.* (1989) used the MINTEQA2 code to model the pH-dependent partitioning of 8 cationic constituents by precipitation and/or adsorption on a sandy aquifer material in an oxidizing environment. The constituents of interest included barium, beryllium, cadmium, copper, nickel, lead, thallium, and zinc. Adsorption of these elements was based on amorphous iron oxide as the only reactive adsorption surface and calculated using the diffuse layer model (DLM). The adsorption parameters and associated reactions for the diffuse layer model were taken from Dzombak (1986). The modeling results were compared to laboratory data for the aquifer material spiked with the trace metals. The predicted concentrations based on the diffuse layer model for adsorption of lead, nickel, and zinc, provided a good description of the pH behavior observed for the spiked samples. The concentrations of the other trace metals were not adequately predicted by the model. These differences were attributed to limitations in the model and/or available thermochemical data.

Turner *et al.* (1993) used the TLM in MINTEQA2 code to model adsorption data for U(VI) on goethite [ $\alpha$ -FeO(OH)]. The FITEQL code was used for adsorption parameter optimization. Their study illustrates the extensive parameter-fitting process that the user must complete to use complex electrostatic adsorption models, such as the TLM.

#### 5.2.6.2 Application to Evaluation of $K_d$ Values

Chemical reaction models *cannot be used to predict a  $K_d$  value*. The user must supply the adsorption parameters when using any of the adsorption model options. Typically, the data required to derive the adsorption parameters needed as input for adsorption submodels in chemical reaction codes are more extensive than information reported in a laboratory batch  $K_d$  study. However, if the parameters have been determined for a particular constituent for a surface complexation model, a chemical reaction model, such as MINTEQA2, can be used to calculate the masses of a constituent that are dissolved or adsorbed and how changes in geochemical conditions, such as pH, affect its adsorption behavior. The user can then derive a  $K_d$  using the calculated dissolved and adsorbed masses of the constituent.

The EPA (EPA, 1992a, 1996) has used the MINTEQA2 model and this approach to estimate  $K_d$  values for several metals under a variety of geochemical conditions and metal concentrations to

support several waste disposal issues. The EPA in its “Soil Screening Guidance” determined MINTEQA2-estimated  $K_d$  values for barium, beryllium, cadmium, Cr(III), Hg(II), nickel, silver, and zinc as a function of pH assuming adsorption on a fixed mass of iron oxide (EPA, 1996; RTI 1994). The calculations assumed equilibrium conditions, and did not consider redox potential or metal competition for the adsorption sites. In addition to these constraints, EPA (1996) noted that this approach was limited by the potential sorbent surfaces that could be considered and availability of thermodynamic data. Their calculations were limited to metal adsorption on iron oxide, although sorption of these metals to other minerals, such as clays and carbonates, is well known.

The data needed to use surface complexation adsorption models are more extensive than those from  $K_d$  studies. More importantly, the data for surface complexation models are based on adsorption on pure mineral phases, such as  $\alpha$ - $\text{Al}_2\text{O}_3$ ,  $\gamma$ - $\text{Al}_2\text{O}_3$ , böhmite, goethite, magnetite, lepidocrocite, ferrihydrite,  $\text{SiO}_2$ , biotite, or kaolinite. Natural soils are more complicated, commonly containing mixtures of more than 10 pure minerals and amorphous mineral coatings. Unless a user can technically defend the assumption that the adsorption of a specific contaminant is dominated in a specific soil-water system, for example, by goethite reactive surfaces, the user is still left with the challenge of extrapolating these modeling results for pure mineral substrates to complex heterogeneous soil-water systems. This issue has been and will continue to be the subject of intensive study, but is not likely to be resolved in the short term or impact contaminant migration and risk assessment modeling soon.

### 5.2.7 MINTEQA2 Databases

The MINTEQA2 model includes an extensive thermodynamic database that is integrated with the aqueous speciation, solubility, and precipitation/dissolution submodels. The content and equations governing the values stored in the thermodynamic database are described below. MINTEQA2 does not have per se an integrated adsorption submodel database. The adsorption reactions and associated model parameters are supplied by the user as part of each input file. However, as discussed below, the current MINTEQA2 software package is supplied with a limited data file for the diffuse layer model (DLM).

#### 5.2.7.1 Thermodynamic Database

The MINTEQA2 thermodynamic database is considered by many to be one of the most extensive databases for modeling the aqueous speciation and solubility of contaminants and geologically-significant constituents (*e.g.*, magnesium, silica, aluminum, *etc.*) in low-temperature, soil-water systems. To understand the fundamental data needs for a thermodynamic database of a chemical reaction code, the basic equations underlying the thermodynamic parameters stored in the MINTEQA2 thermodynamic database will be reviewed in the next section. The content of the MINTEQA2 thermodynamic database as distributed by EPA will be reviewed and then compared relative to the priority constituents considered in the scope of work for this project.

### 5.2.7.1.1 Basic Equations

Thermodynamic data used by MINTEQA2 are stored in the form of equilibrium constants ( $K_{r,298}^{\circ}$ ) and enthalpies (heats) of reaction ( $\Delta H_{r,298}^{\circ}$ ) for aqueous speciation, oxidation/reduction, mineral solubility, and gas solubility reactions. The reference temperature for the MINTEQA2 database, as with most geochemical models, is 298 K (25 °C). Equilibrium constants ( $\log K_{r,T}^{\circ}$ ) may be based on values that have been experimentally-determined or calculated from Gibbs free energies of reaction ( $\Delta G_{r,T}^{\circ}$ ) units of cal/mol according to the equation:

$$\log K_{r,T}^{\circ} = \frac{-\Delta G_{r,T}^{\circ}}{2.303 R T} \quad (5.5)$$

where  $T$  = temperature in degrees Kelvin,  
 $R$  = gas constant (1.9872 cal/mol·K)

Values for  $\Delta G_{r,T}^{\circ}$  are calculated from published values for the Gibbs free energy of formation ( $\Delta G_{f,298}^{\circ}$ ) for each product and reactant in the aqueous speciation or solubility reaction by the equation:

$$\Delta G_{r,298}^{\circ} = \sum \Delta G_{f,298}^{\circ} (\text{products}) - \sum \Delta G_{f,298}^{\circ} (\text{reactants}) . \quad (5.6)$$

To calculate aqueous speciation and solubilities at temperatures other than 25°C, the equilibrium constants are recalculated by the MINTEQA2 code to the temperature  $T$  of interest using the van't Hoff relation:

$$\log K_{r,T}^{\circ} = \log K_{r,298}^{\circ} - \frac{\Delta H_{r,298}^{\circ}}{2.303 R} \left( \frac{1}{T} - \frac{1}{298} \right) . \quad (5.7)$$

Values for enthalpies of reaction are calculated from published enthalpy of formation values ( $\Delta H_{f,298}^{\circ}$ ) using the equation:

$$\Delta H_{r,298}^{\circ} = \sum \Delta H_{f,298}^{\circ} (\text{products}) - \sum \Delta H_{f,298}^{\circ} (\text{reactants}) . \quad (5.8)$$

Values for  $\Delta H_{r,298}^{\circ}$  cannot be calculated for some reactions, because  $\Delta H_{f,298}^{\circ}$  values have not been determined for 1 or more reaction products and/or reactants. In these cases, the MINTEQA2 code assumes that

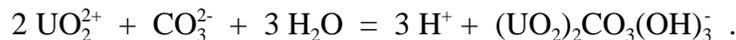
$$\log K_{r,T}^{\circ} \approx \log K_{r,298}^{\circ} . \quad (5.9)$$

Because of the limitations in using the van't Hoff relation for extrapolations over a wide range of temperature, applications of the MINTEQA2 code are limited to temperatures less than 100°C.

### 5.2.7.1.2 Structure of Thermodynamic Database Files

Typically, each aqueous species, redox, mineral, and gas solubility reaction is represented by 2 fix-formatted lines in the thermodynamic database files supplied with MINTEQA2. A third line is sometimes included when the stoichiometry of a reaction is complex. The first file line includes the identification number, formula descriptor,  $\Delta H_{r,298}^{\circ}$  (if available),  $\log K_{r,298}^{\circ}$ , charge, and related data for each reaction. The second line includes the reaction stoichiometry information formulated in terms of the MINTEQA2 components. Each reaction is entered as a formation reaction; that is, the components react to form the “more complex” species, such as an aqueous complex or mineral phase. The hydrogen stoichiometric component of each reaction is balanced with the components  $H^+$  and  $H_2O$ . The hydroxyl species,  $OH^-$ , is not used as a component, but is “formed” in a separate reaction in MINTEQA2.

Based on the protocol used for the MINTEQA2 thermodynamic database, the formation reaction for the uranyl mixed hydroxide/carbonate aqueous species,  $(UO_2)_2CO_3(OH)_3^-$ , is



The corresponding entry in the MINTEQA2 database (in fixed format fields) for this reaction and its associated thermochemical data is

```
8931405 UO2)2CO3OH)3 -14.3940 -0.8969 0.000 0.000-1.00 4.00 0.00 651.0868
2.00 4 2.000 893 1.000 140 3.000 2 -3.000 330
```

For more detailed format information on the MINTEQA2 database files, the reader is referred to the documentation in Allison *et al.* (1991, Appendix A).

### 5.2.7.1.3 Database Components

The thermodynamic database in the original MINTEQ code (Felmy *et al.*, 1984) was taken from the WATEQ3 code (Ball *et al.*, 1981a). Therefore, many of the inorganic reactions and associated thermodynamic values in the MINTEQA2 database can be traced back to the database supplements and sources described in publications documenting the WATEQ series of chemical reactions codes (Ball *et al.*, 1981a, WATEQ2; Ball *et al.*, 1981b, WATEQ3; Plummer *et al.*, 1976, WATEQ; Truesdell and Jones, 1973, WATEQ; Truesdell and Jones 1974, WATEQ).

The thermodynamic database of the current version of MINTEQA2 includes the original MINTEQ database plus modifications and additions completed on contracts with EPA funding. Some of these supplements include, for example, those completed at PNNL, such as the addition of reactions for aqueous species, gases, and solids containing cyanide and antimony by Sehmel

(1989) and those containing chromium, mercury, selenium, and thallium by Deutsch and Krupka.<sup>1</sup> Documentation for these database supplements are not listed in Brown and Allison (1987, MINTEQA1) or Allison *et al.* (1991, MINTEQA2), and may not be publicly available.

The elements for which the MINTEQA2 thermodynamic database has aqueous speciation, mineral solubility, and/or gas solubility reactions are listed in Table 5.3. The second and third columns of this table list the component species used for these elements and the redox reactions, if any, included in MINTEQA2 for different valence states of a particular element. The reader should note that the database does not contain reactions and associated thermodynamic values for specific isotopes of a particular element. The calculated reactions for a soil-water system assumes the total mass of each element.

Although the list of elements in Table 5.3 is substantial, this table and/or a listing of the database files does not indicate if the database of a chemical reaction code, especially for key contaminants, is adequate (*i.e.*, completeness of reactions and quality of associated thermodynamic values) and up-to-date. The user essentially has this important responsibility. One should expect that, as the period of time between the publication of a code's documentation and its use in an application study increases, the thermodynamic database becomes dated and revisions may be warranted.

Table 5.4 lists the organic ligands for which the MINTEQA2 thermodynamic database has aqueous speciation reactions.<sup>2</sup> Because of the limited availability of thermodynamic data for metal-organic complexes important to contaminated soil-water systems, as compared to inorganic aqueous complexes, the MINTEQA2 database, as with all chemical reaction codes, is limited. It does not contain complexation reactions for all metals with each of the organic ligands listed in Table 5.4. The reader will need to do a computer search of the MINTEQA2 ASCII file containing these reactions to determine the extent of the organic complexation reactions for each metal.

#### 5.2.7.1.4 Status Relative to Project Scope

The contaminants chosen for study in this project include chromium, cadmium, cesium, tritium (<sup>3</sup>H), lead, plutonium, radon, strontium, thorium, and uranium. Because the MINTEQA2 thermodynamic database does not contain reactions for specific isotopes, an appraisal of the database content to aqueous speciation and solubility reactions containing tritium is not

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<sup>1</sup> Deutsch, W. J., and K. M. Krupka. September 1985. MINTEQ Geochemical Code: Compilation of Thermodynamic Database for the Aqueous Species, Gases, and Solids Containing Chromium, Mercury, Selenium, and Thallium. Unpublished report prepared by Pacific Northwest Laboratory for the U.S. Environmental Protection Agency in Athens, Georgia.

<sup>2</sup> Although important to contaminant disposal and remediation activities (*i.e.*, "mixed wastes") in the United States, computer modeling of the complexation of contaminant metals with organic complexes was excluded from the scope of the current project due to funding limits.

appropriate. As will be discussed in Volume II of this report, the concentrations of dissolved tritium will be affected by exchange reactions involving hydrogen-containing species dissolved in the soil-water system.

Of the remaining elements, the MINTEQA2 thermodynamic database contains aqueous speciation and solubility reactions for chromium, including the valence states Cr(II), Cr(III), and Cr(VI); cadmium; lead; strontium; and uranium, including the valence states U(III), U(IV), U(V), and U(VI). Except for uranium, the adequacy of the database for these listed elements is not known. Data supplied by Deutsch and Krupka<sup>1</sup> in 1985 is the probable basis for the chromium reactions and associated thermodynamic data. The reactions for cadmium, lead, and strontium may be those taken from the WATEQ-series of codes and supplied with the original MINTEQ code by Felmy *et al.* (1984). It is not known if these have been revised or supplemented since that time.

The reactions and associated thermodynamic data for uranium aqueous species and solid phases were those supplied with the original MINTEQ code. They were taken from those added to WATEQ3 (Ball *et al.*, 1981a) and are based primarily on the compilation of uranium thermodynamic data by Langmuir (1978). Langmuir's review has been superseded by the comprehensive review and compilation of uranium thermodynamic data given in Wanner and Forrest (1992). This compilation represents a significant improvement and update to the values in Langmuir *et al.* (1978), including for U(VI) carbonate and hydrolysis species that are important in soil-water systems with pH values greater than 5.

Of the elements included in the project scope, the thermodynamic database distributed by EPA with MINTEQA2 does not contain reactions and associated thermodynamic data for aqueous species and solids containing cesium, plutonium, radon, and thorium. Published compilations of thermodynamic data for aqueous species, solids, and gases containing these elements are available, such as an Langmuir and Herman (1980), Lemire and Tremaine (1980), Peterson *et al.* (1987b), Phillips *et al.* (1988), Smith and Martell (1976 and more recent supplements), Smith *et al.* (1997), Wagman *et al.* (1982), and others. These sources can be used as good starting points for adding reactions for cesium, plutonium, radon, and thorium to the MINTEQA2 database. However, because these sources are becoming dated, additional reviews of the more recent thermodynamic literature would be needed to supplement them and generate more up-to-date compilations for these elements. Other compilations of thermodynamic data for these elements include databases compiled by geochemical modeling groups elsewhere in the United States and other countries. When documented, these databases are useful sources of information.

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<sup>1</sup> Deutsch, W. J., and K. M. Krupka. September 1985. MINTEQ Geochemical Code: Compilation of Thermodynamic Database for the Aqueous Species, Gases, and Solids Containing Chromium, Mercury, Selenium, and Thallium. Unpublished report prepared by Pacific Northwest Laboratory for the U.S. Environmental Protection Agency in Athens, Georgia.

**Table 5.3.** Component species in MINTEQA2 thermodynamic database.

Element	Component Species	Valence States
Ag	Ag <sup>+</sup>	
Al	Al <sup>3+</sup>	
As	H <sub>3</sub> AsO <sub>3</sub> <sup>o</sup> (aq), H <sub>3</sub> AsO <sub>4</sub> <sup>o</sup> (aq)	As(III), As(V)
B	H <sub>3</sub> BO <sub>3</sub> <sup>o</sup> (aq)	
Ba	Ba <sup>2+</sup>	
Br	Br <sup>-</sup>	
C	CO <sub>3</sub> <sup>2-</sup> , CN <sup>-</sup> , OCN <sup>-</sup>	
Ca	Ca <sup>2+</sup>	
Cd	Cd <sup>2+</sup>	
Cl	Cl <sup>-</sup>	
Cr	Cr <sup>2+</sup> , Cr(OH) <sub>2</sub> <sup>+</sup> , CrO <sub>4</sub> <sup>2-</sup>	Cr(II), Cr(III), Cr(VI)
Cu	Cu <sup>+</sup> , Cu <sup>2+</sup>	Cu(I), Cu(II)
F	F <sup>-</sup>	
Fe	Fe <sup>2+</sup> , Fe <sup>3+</sup>	Fe(II), Fe(III)
Electron	e <sup>-</sup>	
H	H <sup>+</sup> , H <sub>2</sub> O (l)	
Hg	Hg <sub>2</sub> <sup>2+</sup> , Hg(OH) <sub>2</sub> <sup>o</sup> (aq)	Hg(I), Hg(II)
I	I <sup>-</sup>	
K	K <sup>+</sup>	
Li	Li <sup>+</sup>	
Mg	Mg <sup>2+</sup>	

**Table 5.3.** Continued.

<b>Element</b>	<b>Component Species</b>	<b>Valence States</b>
Mn	$\text{Mn}^{2+}$ , $\text{Mn}^{3+}$	Mn(II), Mn(III)
N	$\text{NH}_4^+$ , $\text{NO}_2^-$ , $\text{NO}_3^-$ , $\text{CN}^-$ , $\text{OCN}^-$	N(-III), N(III), N(V)
Na	$\text{Na}^+$	
Ni	$\text{Ni}^{2+}$	
P	$\text{PO}_4^{3-}$	
Pb	$\text{Pb}^{2+}$	
Rb	$\text{Rb}^{2+}$	
S	$\text{HS}^-$ , $\text{S}^\circ$ , $\text{SO}_4^{2-}$	S(-II), S(VI)
Sb	$\text{Sb(OH)}_3^\circ$ (aq), $\text{Sb(OH)}_6^-$	Sb(III), Sb(V)
Se	$\text{HSe}^-$ , $\text{HSeO}_3^-$ , $\text{SeO}_4^{2-}$	Se(-II), Se(IV), Se(VI)
Si	$\text{H}_4\text{SiO}_4^\circ$ (aq)	
Sr	$\text{Sr}^{2+}$	
Tl	$\text{Tl}^+$ , $\text{Tl(OH)}_3^\circ$ (aq)	Tl(I), Tl(III)
U	$\text{U}^{3+}$ , $\text{U}^{4+}$ , $\text{UO}_2^+$ , $\text{UO}_2^{2+}$	U(III), U(IV), U(V), U(VI)
V	$\text{V}^{2+}$ , $\text{V}^{3+}$ , $\text{VO}^{2+}$ , $\text{VO}_2^+$	V(II), V(III), V(IV), V(V)
Zn	$\text{Zn}^{2+}$	

**Table 5.4.** Organic ligands in MINTEQA2 thermodynamic database.

<b>Organic Constituents / Complexants</b>	
acetate	methylamine
butyrate	2-methyl pyridine
iso-butyrate	3-methyl pyridine
citrate	4-methyl pyridine
diethylamine	n-butylamine
dimethylamine	nitrilotriacetate <sup>3-</sup>
EDTA <sup>4-</sup>	phthalate
ethylenediamine	propanoate
formate	salicylate
fulvate	tartrate
glutamate	tri-methylamine
glycine	tributylphosphate
hexylamine	valerate
humate	iso-valerate
iso-propylamine	
n-propylamine	

It should be noted that the thermodynamic database distributed with EPA's MINTEQA2 software package does not include reactions and thermodynamic data for aqueous species and solids containing americium, cobalt, neptunium, niobium, radium, and technetium. Although these radionuclides are not part of the scope of this project, they may be important with respect to contamination and remediation at some sites in the United States and/or performance assessments of proposed LLW and HLW disposal facilities or decommissioning sites. Except for niobium, published compilations of thermodynamic data for these elements, especially for americium (Silva *et al.*, 1995) and technetium (Rard, 1983), exist that can be used to supplement the MINTEQA2 database. The thermodynamic data for aqueous species and solids containing niobium are extremely limited which precludes adequate modeling of aqueous/solid phase equilibria for niobium in soil-water systems.

The thermodynamic database of MINTEQA2 was augmented by Krupka and Serne (1998) for aqueous species and solids containing several radionuclide elements of interest to NRC. These database modifications were based on data files provided by D. Turner<sup>1</sup> who had added these

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<sup>1</sup> Center for Nuclear Waste Regulatory Analyses (CNWRA), Southwest Research Institute, San Antonio, Texas

reactions and thermodynamic data to his version of MINTEQA2. The database additions included MINTEQ-formatted reactions, associated thermodynamic data (*i.e.*,  $\log K_{r,298}^{\circ}$  and  $\Delta H_{r,298}^{\circ}$ ) and ancillary information (*e.g.*, identification number, formula, charge, mass, reaction stoichiometry) for aqueous species and solids containing americium, neptunium, plutonium, radium, technetium, thorium, and uranium. The database changes for uranium are based on the compilation by Wanner and Forest (1992), and supersede those listed in the MINTEQA2 database as obtained from EPA. Additional revisions to the thermodynamic data for these radionuclide elements were identified by Krupka and Serne (1998) and added to the MINTEQA2 files. These database modifications have not undergone an in depth examination relative to quality-assurance considerations.

#### 5.2.7.1.5 Issues Related to Database Modifications

Successful application of chemical reaction models to quantify contaminant release and transport in soil-water systems is dependent on the development of adequate and internally consistent thermodynamic databases. The thermodynamic databases of chemical reaction codes are typically revised or supplemented based on specific project needs and the availability of thermodynamic data for aqueous species, gases, and solids containing the constituents of interest.

Although an extensive number of tabulations and critical reviews [*e.g.*, see references in Serne *et al.* (1990, Table 3.2)] of thermodynamic data for inorganic complexes and solids have been published during the last 20 years, the selection of "best" values from these publications is a technically and logistically challenging effort. Some of the issues and problems associated with the selection of thermodynamic data are described in detail in Potter (1979), Nordstrom and Munoz (1985), and Smith and Martell (1995). The critical evaluation and selection of a thermodynamic database requires an understanding of general solution chemistry and the phase assemblages of minerals and related amorphous solids associated with a particular cationic and/or anionic constituent. The investigator developing the model's database must also be cognizant of the criteria initially used to review and select the original data for the published tabulations.

Because thermodynamic data tabulations usually contain an inadequate amount of reviewed thermodynamic data for aqueous species of trace metals, available tabulations are typically deficient for modeling contaminated soil-water systems. Researchers are thus faced with the difficult responsibility of assembling thermodynamic data from other possibly less-credible publications, borrowing values from extant chemical reaction models, and/or conducting their own reviews of published thermodynamic data. Because there is a growing reliance on thermodynamic review efforts completed by coworkers and other research organizations, documentation supporting these reviews and the rationale for selecting each datum that is "accepted" for a model's database are extremely important with respect to (1) defining the credibility of the database, (2) achieving an internally consistent database, (3) minimizing duplication in future review efforts, and (4) describing the selection criteria and calculation methods used in selecting the best values.

### 5.2.7.2 Sorption Database

The MINTEQA2 code is not designed to have a thermochemical database, analogous to the thermodynamic database, that is integrated with the adsorption submodel and its 7 model options. The adsorption reactions and associated model parameters need to be supplied by the user as part of each input file. This process and example input files are discussed in Allison *et al.* (1991).

However, the current MINTEQA2/PRODEFA2 software package is supplied with a limited adsorption data file for use with the diffuse layer adsorption model option. Data files are not supplied for any of the other adsorption model options. The data file, formatted in ASCII, is named *FEO-DLM.dbs*. It includes surface reactions and associated intrinsic conditional surface complexation constants applicable to the diffuse layer model for the adsorption of the trace metals  $\text{Ba}^{2+}$ ,  $\text{Be}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Zn}^{2+}$ , and the ligands  $\text{H}_3\text{AsO}_3^\ominus$  (aq),  $\text{H}_3\text{AsO}_4^\ominus$  (aq),  $\text{H}_3\text{BO}_3^\ominus$  (aq),  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$  onto 2 types of iron-oxide sites. The adsorption constants are based on data published by Dzombak (1986).<sup>1</sup>

#### 5.2.7.2.1 Status Relative to Project Scope

Of the elements chosen for study in this project, cadmium and lead are the only 2 elements included in the diffuse layer adsorption model data file supplied with MINTEQA2. As mentioned above, this file is restricted to adsorption onto 2 types of iron-oxide sites, and is therefore not applicable for the adsorption of these metals to other mineral reactive surfaces. None of the other contaminants, including chromium, cesium, plutonium, radon, strontium, thorium, or uranium, are supported by this data file.

The MINTEQA2/PRODEFA2 software package includes no adsorption database files for the activity partition coefficient ( $K_d^{\text{act}}$ ), activity Langmuir isotherm, activity Freundlich isotherm, ion exchange, constant capacitance, or triple layer adsorption models.

#### 5.2.7.2.2 Published Database Sources

No published compilations are known to exist for adsorption constants for the activity partition coefficient ( $K_d^{\text{act}}$ ), activity Langmuir isotherm, activity Freundlich isotherm, and ion exchange adsorption models used in MINTEQA2. Numerous individual data sets have been published for the adsorption of many individual contaminants on specific mineral substrates, such as  $\text{TiO}_2$  or goethite. Typically, these data are parameterized using 1 or more of the surface complexation models. Compilations and review of these studies was beyond the scope of this project.

Smith and Jenne (1988) (and related papers by Dzombak and Hayes, 1992, and Smith and Jenne, 1992) compiled and evaluated published values for triple layer model constants for the adsorption

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<sup>1</sup> Personal communication from N. T. Loux at the U.S. Environmental Protection Agency in Athens, Georgia.

of numerous constituents on  $\alpha$ -FeO(OH), amorphous iron(III) hydrous oxide, and  $\delta$ -MnO<sub>2</sub> solids. This study was conducted for the U.S. Environmental Protection Agency (Athens, Georgia) for use in modeling the migration of contaminants in ground-water systems. Their compilation included intrinsic constants and associated reaction stoichiometries for the adsorption of species containing the following constituents:

- For adsorption onto Fe(III) hydrous oxides: Ag, As(V), Ba, CO<sub>3</sub>, Ca, Cd, Co, Cr(VI), Cu(II), Fe(II), Hg(II), Mg, Mn(II), Np(V), Pb, Pu(IV), Sb(III), Sb(V), Se(VI), Se(IV), S, SO<sub>4</sub>, Th(I), U(VI), and Zn
- For adsorption onto  $\delta$ -MnO<sub>2</sub>: Ag, Ba, Ca, Cd, Co, Cu(II), Fe(II), Hg(II), Mg, Mn(II), Pb, Th(I), and Zn.

Turner (1995) compiled and critically reviewed adsorption data reported in the literature for surface complexation models. He then used a uniform approach to parameterize these data using the diffuse layer, constant capacitance, and triple layer surface complexation models. His study was conducted in support of research funded by NRC to study the potential migration of radionuclides associated with the geologic disposal of commercial high level radioactive waste. Turner (1993) previously described the use of the MINTEQA2 chemical reaction code to model adsorption of radionuclides. Turner (1995) reported model constants for:

- Americium(III) on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and amorphous SiO<sub>2</sub>
- Neptunium(V) on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, boehmite ( $\gamma$ -AlOOH), goethite [ $\alpha$ -FeO(OH),] magnetite (Fe<sub>3</sub>O<sub>4</sub>), lepidocrocite [ $\gamma$ -FeO(OH)], ferrihydrite (5Fe<sub>2</sub>O<sub>3</sub> · 9H<sub>2</sub>O), amorphous SiO<sub>2</sub>, biotite mica [K(Mg,Fe)<sub>3</sub>(Al,Fe)Si<sub>3</sub>O<sub>10</sub>(OH,F)<sub>2</sub>], and kaolinite [Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>]
- Plutonium(IV) on goethite
- Plutonium(V) on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and goethite
- Thorium on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and amorphous SiO<sub>2</sub>
- Uranium(VI) on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, magnetite, ferrihydrite, goethite, quartz (SiO<sub>2</sub>), and kaolinite
- Carbon on ferrihydrite.

We are not aware of any other major published compilations of adsorption thermochemical data for use with MINTEQA2. Moreover, it is very possible that individual investigators have compiled and parameterized their own databases of adsorption constants based on the needs of their individual research projects. General access, especially in these days of cost recovery, and quality assurance issues will likely prohibit the use of many such individual data files.

### 5.3 Adsorption Model Options in MINTEQA2

The MINTEQA2 chemical reaction code includes 7 adsorption model options. Each of these adsorption models and their associated equations and reactions are briefly described below. MINTEQA2 includes the following non-electrostatic adsorption models

- Activity partition coefficient ( $K_d^{\text{act}}$ ) model
- Activity Langmuir model
- Activity Freundlich model
- Ion exchange model

and electrostatic adsorption models

- Diffuse layer model
- Constant capacitance model
- Triple layer models.

The following descriptions and associated equations are adapted from the MINTEQA2 documentation by Allison *et al.* (1991). When using the adsorption model options, readers are cautioned to read the MINTEQA2 documentation carefully relative to correct entry and formulation of model reactions and associated constants.

It should be noted that the non-electrostatic models in MINTEQA2 are formulated in terms of species activities, and not the more traditional approach of total concentrations of dissolved metal. The purpose of this approach is to reduce the dependency of the model parameters to effects from ionic strength and aqueous complexation of the adsorbing metal.

Limitations remain, however, regarding these activity formulations which restricts the range of applicability of these non-electrostatic models. These non-electrostatic adsorption models do not consider: charge balance on surface sites and adsorbed species, electrostatic forces between the adsorbing species and charged surface of the mineral, and reactions between the mineral and dissolved constituents other than the adsorbing metal. The effect of these processes changes with variations in the composition of an aqueous solution. These processes are, however, incorporated into the more robust, but more data intensive, electrostatic “surface complexation” adsorption models. The following descriptions of the electrostatic adsorption models incorporated into MINTEQA2 are cursory. The reader is referred to sources, such as Westall and Hohl (1980), Morel *et al.* (1981), Barrow and Bowden (1987), and Davis and Kent (1990), for detailed descriptions, comparisons, and derivations of the relevant equations and reactions associated with these models.

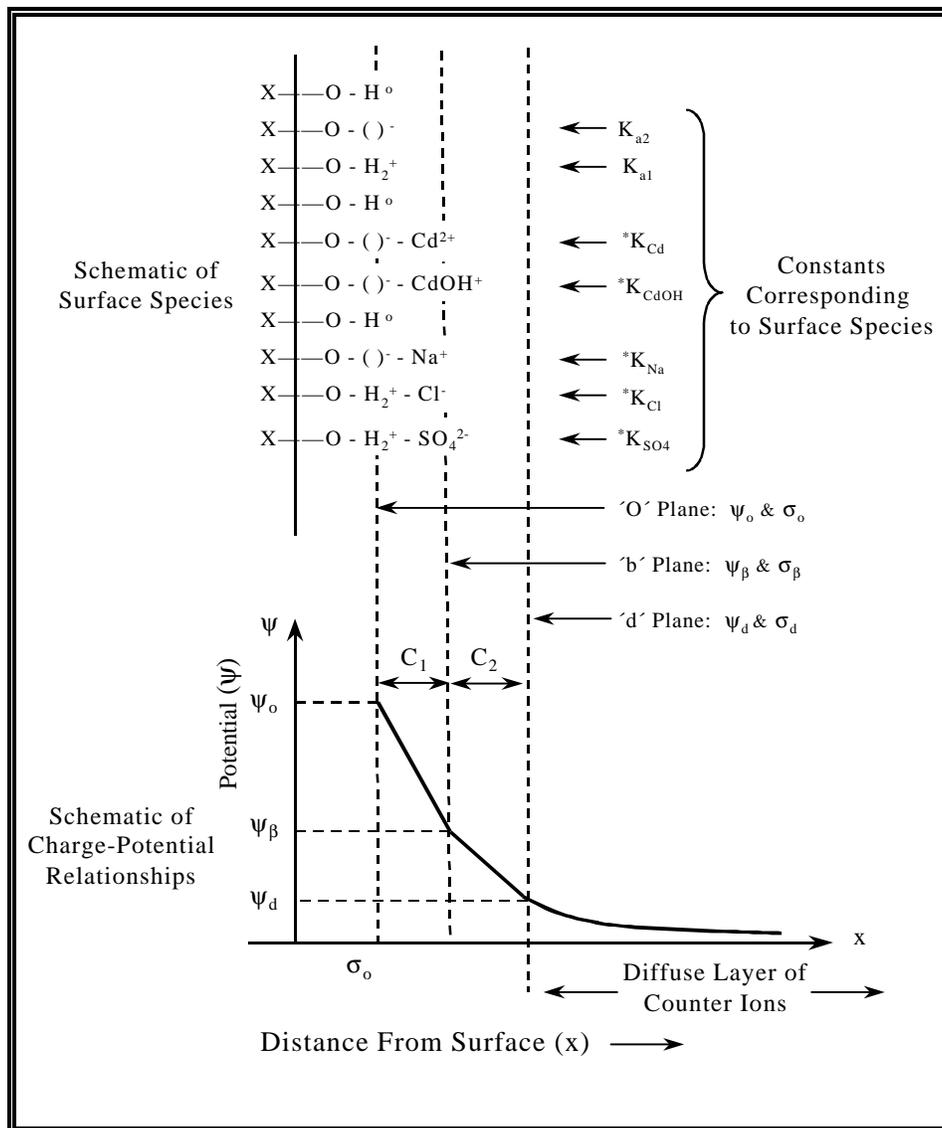
### 5.3.1 *Electrostatic Versus Non-Electrostatic Models*

Hydrous oxides of iron, manganese, and aluminum and amorphous aluminosilicates that exist as discrete mineral grains or surface coatings on other minerals in soils are assumed to be primary adsorbents for trace metals ions. These solid phases have variable surface charges and exhibit amphoteric behavior. The solids have a net positive charge at pH values below their point of zero charge (PZC) and a net negative charge at pH values above the PZC (see Chapter 2).

These surface charges create electrostatic potentials extending into the surrounding solutions. Dissolved aqueous species that have a charge of the same polarity as the surface will be repelled, while aqueous species with a charge opposite to that of the surface will be attracted (adsorbed). The electrostatic potentials associated with charged surfaces may therefore affect the adsorption of dissolved species on these surfaces. Unlike the non-electrostatic adsorption models, the electrostatic models include a component that accounts for the electrostatic potentials at the charged surface. The mass action equations of electrostatic adsorption models include terms that modify the activities of adsorbing species approaching charged surfaces by the electrical work necessary to penetrate the zone of electrostatic potentials ( $\psi$ 's) associated with the mineral surface. The 3 electrostatic models in MINTEQA2 differ primarily in the types of surface species that are allowed within specific physical locations or layers extending away from the surface and in the parameters that each model uses.

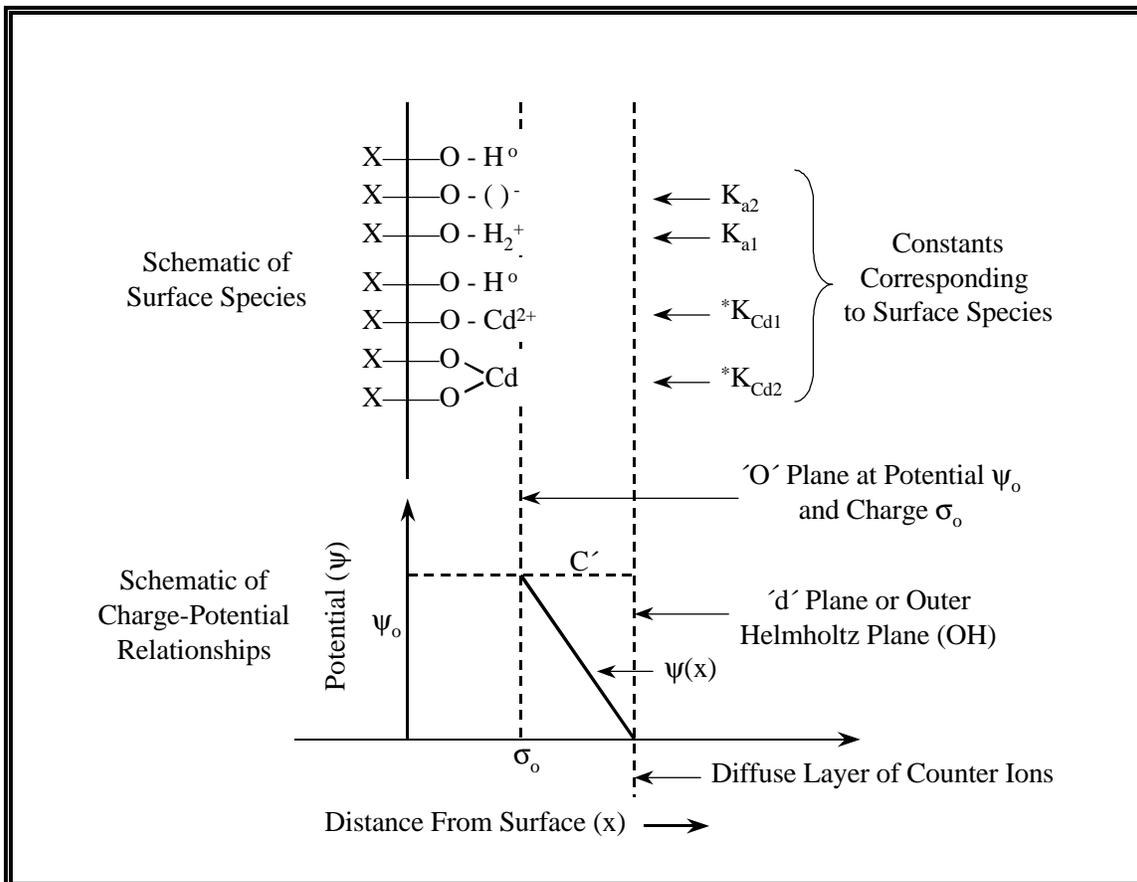
The 3 electrostatic models in MINTEQA2 deal with adsorption as surface complexation reactions analogous to aqueous complexation reactions in solution. In the descriptions of the MINTEQA2 adsorption models that follow, surface sites are represented in the adsorption reactions and mass action expressions as SOH groups, where S refers to the mineral structure and adsorption site located at the solid-liquid interface. Some ions, such as  $H^+$ ,  $OH^-$ , and a variety of trace metal ions are assumed to be adsorbed by complexation with these surface sites.

In the triple layer model (TLM), the most complicated of the 3 electrostatic adsorption models in MINTEQA2, the space around the solid surface is represented in surface complexation adsorption models as 3 semi-infinite layers or zones between the solid surface and the solution (Figure 5.4). These zones are separated by the  $\alpha$ ,  $\beta$ , and  $d$  planes. Starting at the mineral surface, The  $\alpha$  plane represents the first interface between the solid surface and the aqueous phase. Generally, only the  $H^+$  and  $OH^-$  ions are allowed to penetrate the  $\alpha$  layer to interact with the solid surface. Beyond the  $\alpha$  plane, farther from the mineral surface, is the  $\beta$  plane which ends at the boundary of the diffuse zone, the  $d$  plane. Dissolved ions, such as macro constituents (*e.g.*,  $Na^+$ ,  $Ca^{2+}$ , and  $SO_4^{2-}$ ) and trace constituents ions that are adsorbing onto the solid surface are allowed into the  $\beta$  layer. The third layer is the diffuse zone where the ions are not influenced strongly by electrostatic charge on the solid surface. The ions in this region are considered to be counterions that neutralize any residual charge caused by the surface and adsorbed ions in the  $\beta$  layer. Continuing further from the mineral surface, the  $d$  layer blends into the bulk solution.



**Figure 5.4.** Schematic representation of the triple layer model showing surface species and surface charge-potential relationships. [Taken from Peterson *et al.* (1987a). Brackets in the *o* plane indicated deprotonated surface sites.]

The conceptual models for the constant capacitance (Figure 5.5) and diffuse layer models are simplified to only 2 zones separated by the  $o$  and  $d$  planes. The difference between these 2 adsorption models is in the function relating total surface charge,  $T_o$ , to surface potential  $\psi_o$  (discussed in Sections 5.3.6 and 5.3.7). This function [ $\psi(x)$  in Figure 5.5)] is linear and exponential, respectively, in the constant capacitance and diffuse layer models. It should be noted that parameters subscripted with “ $o$ ” in that 2-layer models are not equivalent to the  $o$  plane parameters defined for the triple layer model due to differences in the definition of the  $o$  plane.



**Figure 5.5.** Schematic representation of the constant capacitance layer model showing surface species and surface charge-potential relationships. [Taken from Peterson *et al.* (1987a). Brackets in the  $o$  plane indicated deprotonated surface sites.]

In all 3 models, a charge,  $\sigma$ , associated with the surface is assumed to be balanced by a charge ( $\sigma_d$ ) associated with the diffuse layer  $d$  of counterions such that

$$\sigma + \sigma_d = 0 . \quad (5.10)$$

In the constant capacitance and diffuse-layer models, all adsorbed ions contribute to the surface charge. However, the net charge  $\sigma$  due to adsorption in the triple layer model is the sum of the charges associated with 2 rather than 1 adsorbing plane. These include the innermost  $\alpha$  plane and the  $\beta$  plane, which are characterized by charges  $\sigma_\alpha$  and  $\sigma_\beta$ , respectively. Thus, for the triple layer model, the net surface charge is given by

$$\sigma_\alpha + \sigma_\beta = \sigma \quad (5.11)$$

which is balanced by the charge in the diffuse layer such that

$$(\sigma_\alpha + \sigma_\beta) + \sigma_d = 0 . \quad (5.12)$$

Because the electrical potential gradients extending away from the mineral's surface result from the surface charge, the specifically adsorbed potential determining ions also govern distributions of counterions in the diffuse layer.

Activities of ions in solution and near the surface are influenced by the presence of electrostatic potentials arising from the surface charge. The activity difference between ions near the surface and those far away is the result of electrical work required to move them across the potential gradient between the charged surface and the bulk solution. The activity change between these zones is related to the ion charge,  $z$ , and the electrical potential,  $\psi$ , near the surface and can be expressed using the exponential Boltzmann expression,

$$\{X_s^z\} = \{X^z\} [e^{-\psi F/RT}]^z \quad (5.13)$$

where  $z$  = charge of ion X,  
 $\{X_s^z\}$  = activity of an ion X of charge  $z$  near the surface,  
 $\{X^z\}$  = activity of ion X in bulk solution beyond the influence of the charged surface,  
 $e^{-\psi F/RT}$  = Boltzmann factor,  
 $F$  = Faraday constant,  
 $R$  = ideal gas constant, and  
 $T$  = absolute temperature in Kelvin.

The general algorithm is similar for all 3 electrostatic models in MINTEQA2. Each model is only briefly described below. The surface reactions for the electrostatic models in MINTEQA2 are written with the Boltzmann factor included as a reactant component with a stoichiometric factor appropriate for the reaction. Although these electrostatically-related components are included in the mass action equations, they are not analogous to the chemical components defined in

MINTEQA2 and have no analytical totals for their input values. Their total charges are determined from equations that are unique to each electrostatic model and potential. The activity coefficients for the Boltzmann factor components are set to unity in MINTEQA2.

Adsorption reactions are entered as part of MINTEQA2 input files. The MINTEQA2 code, as noted previously, has no integrated adsorption database. The adsorption reactions and associated equilibrium constants are written in terms of the neutral surface site, SOH. They are entered as formation reactions, analogous to the aqueous complexation and mineral solubility reactions included in the thermodynamic database. Published adsorption reactions and associated constants are, however, sometimes referenced to the protonated surface site  $\text{SOH}_2^+$  for adsorbing anions and the deprotonated site  $\text{SO}^-$  for adsorbing cations. In these cases, the user must modify the published reaction and equilibrium constant data in terms of MINTEQA2 components to use them in a MINTEQA2 input file.

### 5.3.2 Activity Partition Coefficient ( $K_d$ ) Model

The traditional partition coefficient,  $K_d$ , adsorption model (see Chapter 2) is defined as the ratio of the concentration of metal bound on the surface of the solid to the total concentration of metal dissolved in the liquid phase at equilibrium as in

$$K_d = \frac{\text{Amount of element sorbed on solid} / \text{solid mass}}{\text{Amount of element dissolved in solution} / \text{solution volume}}. \quad (5.14)$$

This process can be expressed as the surface adsorption reaction



where SOH = unreacted surface site,  
M = a dissolved metal M, and  
SOH·M = adsorption site occupied by a component or surface-bound metal M.

The convention used for symbols in the adsorption model equations discussed in this chapter follows that used by Allison *et al.* (1991). Although the basic adsorption equations are comparable to those listed in Chapter 2, the symbols may differ slightly.

The mass action expression for this reaction is

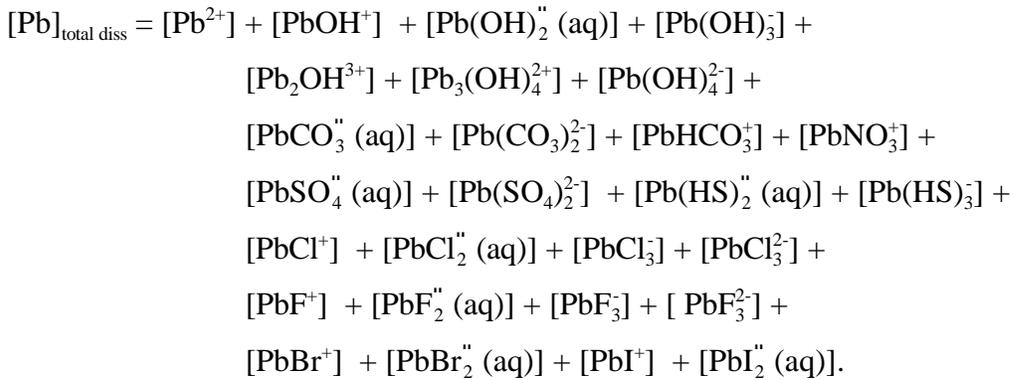
$$K_d = \frac{[\text{SOH}\cdot\text{M}]}{[\text{M}]_{\text{total diss}}} \quad (5.16)$$

where  $[\text{SOH}\cdot\text{M}]$  = concentration of adsorption sites occupied by a component M or surface-bound metal per unit mass of adsorbing solid

$[M]_{\text{total diss}} = \text{total concentration of dissolved M at equilibrium.}$

Following common convention for thermodynamic nomenclature, reaction species indicated within [ ] refer to concentrations, and those indicated within { } refer to activities. Equation 5.16 assumes that the concentration of unreacted surface sites, SOH, are in great excess relative to the total concentration of dissolved metal and the activity of SOH is equal to 1.

As mentioned previously, the traditional  $K_d$  assumes that all species of metal M absorb with equal strength, and  $[M]_{\text{total diss}}$  includes all aqueous species containing metal M. For example, using the species listed in the MINTEQA2 thermodynamic database, the total concentrations of dissolved lead,  $[Pb]_{\text{total diss}}$ , in the absence of any organic complexants in the water, could include the following species:



In the presence of organic complexants,  $[Pb]_{\text{total diss}}$  would also include, in addition to the lead species listed above, the concentrations of aqueous lead citrate, acetate, EDTA, HEDTA, and other organic complexes.

Because experimental data suggest that only certain aqueous species react with the surface of a mineral, the traditional  $K_d$  model is reformulated in MINTEQA2 in terms of the activities of species to provide the activity  $K_d^{\text{act}}$  model.

In MINTEQA2, the mass action expression for the activity  $K_d^{\text{act}}$  model is

$$K_d^{\text{act}} = \frac{\{SOH \cdot M\}}{\{M\}} = \frac{[SOH \cdot M]}{\gamma_M [M]} \quad (5.17)$$

where  $\{M\} =$  free activity of the uncomplexed “bare” cation of M in the equilibrium solution,  
 $\gamma_M =$  activity coefficient of dissolved species M

The quantity  $\{SOH \cdot M\}$  is defined as equal to  $[SOH \cdot M]$ . This assumption is made because there is no generally accepted method for calculating activity coefficients for unreacted or reacted adsorption sites. The parameter  $K_d^{\text{act}}$  can be considered the equilibrium constant for the surface

reaction described in Equation 5.15. This model assumes that there is an unlimited supply of unreacted adsorption sites and the mineral surface cannot become saturated regardless of how much M adsorbs.

### 5.3.3 Activity Langmuir Model

The concentration-based Langmuir adsorption model has the constraint that the number of surface sites available for adsorption is limited. This is the only difference between the Langmuir and  $K_d$  adsorption models. The partition coefficient,  $K_d$ , model is linear with respect to the total concentration of a dissolved metal, whereas the Langmuir model is non-linear. The user must specify the concentration of available adsorption sites as part of the input file. The Langmuir equation for adsorption is defined by

$$[\text{SOH} \cdot \text{M}] = \frac{K_L [\text{SOH}]_{\text{total}} [\text{M}]_{\text{total diss}}}{1 + K_L [\text{M}]_{\text{total diss}}} \quad (5.18)$$

where  $K_L$  = Langmuir adsorption constant,  
 $[\text{SOH} \cdot \text{M}]$  = amount of adsorbed metal M per unit mass of adsorbing solid,  
 $[\text{SOH}]_{\text{total}}$  = total concentration of available surface adsorption sites, and  
 $[\text{M}]_{\text{total diss}}$  = total concentration of dissolved metal M at equilibrium.

The surface adsorption reaction used for the Langmuir model is identical to that for the  $K_d$  model



The equilibrium constant,  $K_L^{\text{act}}$ , for this reaction can be expressed in terms of activities as

$$K_L^{\text{act}} = \frac{\{\text{SOH} \cdot \text{M}\}}{\{\text{M}\} \{\text{SOH}\}} = \frac{\gamma_{\text{SOH} \cdot \text{M}} [\text{SOH} \cdot \text{M}]}{\gamma_{\text{M}} [\text{M}] \gamma_{\text{SOH}} [\text{SOH}]} \quad (5.20)$$

As discussed previously, the activity coefficients pertaining to unreacted and reacted surface sites in this and the other adsorption models in MINTEQA2 are assigned values of unity. Equation 5.20 can then be rewritten as

$$K_L^{\text{act}} = \frac{[\text{SOH} \cdot \text{M}]}{\gamma_{\text{M}} [\text{M}] [\text{SOH}]} \quad (5.21)$$

The mass balance equation for the available surface sites is

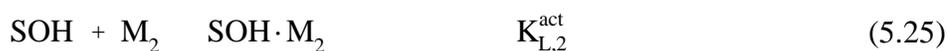
$$[\text{SOH}]_{\text{total}} = [\text{SOH} \cdot \text{M}] + [\text{SOH}] \quad (5.22)$$

By combining Equations 5.21 and 5.22 in terms of  $[\text{SOH}]_{\text{total}}$  and  $[\text{SOH} \cdot \text{M}]$ , one obtains the Langmuir relationship in terms of activities

$$[\text{SOH} \cdot \text{M}] = \frac{K_L^{\text{act}} [\text{SOH}]_{\text{total}} \gamma_m [\text{M}]}{1 + K_L^{\text{act}} \gamma_m [\text{M}]} . \quad (5.23)$$

By substituting  $K_L^{\text{act}}$  with  $K_L$  and setting  $\gamma_m$  to a value of 1, Equation 5.23 reduces to the concentration Langmuir model expressed in Equation 5.18.

To use MINTEQA2 to model competition between different metals for adsorption on the available surface sites, one must define the separate adsorption reactions on the surface. For the competitive Langmuir model for the competing metals  $M_1, M_2, \dots, M_n$ , separate reactions with associated mass balance expressions need to be formulated using Equations 5.19-5.21 such that



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·



Geochemical modeling and plotting techniques may be used to derive constants for the activity Langmuir model from experimentally-measured, concentration-based  $K_L$  data. One must first determine if the concentration-based Langmuir model fits the experimental data by using the linear form of Equation 5.18

$$\frac{[\text{M}]_{\text{total diss}}}{[\text{SOH} \cdot \text{M}]} = \frac{1}{K_L [\text{SOH}]_{\text{total}}} + \frac{[\text{M}]_{\text{total diss}}}{[\text{SOH}]_{\text{total}}} . \quad (5.27)$$

A plot of  $[\text{M}]_{\text{total diss}}/[\text{SOH} \cdot \text{M}]$  versus  $[\text{M}]_{\text{total diss}}$  will result in a straight line with the slope  $1/[\text{SOH}]_{\text{total}}$  and intercept  $1/K_L[\text{SOH}]_{\text{total}}$  if the data fit the Langmuir isotherm. The value for the concentration-based  $K_L$  is obtained by dividing this slope by the intercept. Geochemical modeling is then used to calculate the aqueous speciation of metal M for the composition of the aqueous solution in which the  $K_L$  data were determined. The  $K_L^{\text{act}}$  value can then be derived from an analogous plot in which the calculated activities  $\{M\}$  for metal M are plotted in place of the concentration term  $[M]$ .

### 5.3.4 Activity Freundlich Model

The concentration-based Freundlich equation for adsorption is defined by

$$[\text{SOH}\cdot\text{M}] = K_F [\text{M}]_{\text{total diss}}^{1/N} \quad (5.28)$$

where  $K_F$  = Freundlich adsorption constant,  
 $[\text{SOH}\cdot\text{M}]$  = amount of adsorbed metal M per unit mass of adsorbing solid,  
 $[\text{M}]_{\text{total diss}}$  = total concentration of dissolved metal M at equilibrium, and  
 $N$  = a constant.

The Freundlich equation is sometimes written with the exponent in Equation 5.28 being  $N$  instead of  $1/N$ . The Freundlich model assumes, like the  $K_d$  adsorption model, an unlimited supply of unreacted adsorption sites. For the special case where  $N$  equals 1, the mass action equations for the Freundlich and  $K_d$  models are identical.

The Freundlich model can be considered as a surface adsorption reaction where the stoichiometric coefficient for the adsorbed metal M equals  $1/N$  as in



The equilibrium constant,  $K_F^{\text{act}}$ , for this reaction can be expressed in terms of activities as

$$K_F^{\text{act}} = \frac{\{\text{SOH}\cdot\text{M}\}}{\{\text{M}\}^{1/N} \{\text{SOH}\}} \quad (5.30)$$

Like the activity  $K_d^{\text{act}}$  model, there is no mass balance on surface sites, and, assuming an excess of sites with respect to adsorbed metal M, the concentration,  $[\text{SOH}]$ , and activity  $\{\text{SOH}\}$ , of the unreacted surface sites are assumed equal and set to 1. Under these conditions and assuming  $\{\text{SOH}\cdot\text{M}\}$  equals  $[\text{SOH}\cdot\text{M}]$  as with the activity  $K_d^{\text{act}}$  and Langmuir models, Equation 5.30 becomes

$$K_F^{\text{act}} = \frac{[\text{SOH}\cdot\text{M}]}{\{\text{M}\}^{1/N}} \quad (5.31)$$

which is similar to the  $K_d^{\text{act}}$  model except that the stoichiometric coefficient  $1/N$  of the adsorbing species of metal M.

An approach using geochemical modeling and plotting techniques similar to that described for the activity Langmuir model may be used to calculate constants for the activity Freundlich model from experimentally-measured, concentration-based  $K_F$  data. One must first determine if the Freundlich model fits the experimental data by using the logarithmic form of the Freundlich mass action Equation 5.28

$$\log [\text{SOH}\cdot\text{M}] = \log K_F + \left( \frac{1}{N} \right) \log [\text{M}]_{\text{total diss}} . \quad (5.32)$$

If the data fit the model, a plot of  $\log [\text{SOH}\cdot\text{M}]$  versus  $\log [\text{M}]_{\text{total diss}}$  will result in a straight line with the slope  $1/N$  and intercept  $\log K_F$ . Geochemical modeling is then used to calculate the aqueous speciation of metal  $M$  for the composition of the aqueous solution in which the  $K_F$  data were determined. The  $K_F^{\text{act}}$  value can then be derived by plotting the calculated activities  $\{M\}$  for the adsorbing species of metal  $M$  in place of the concentration term  $[\text{M}]_{\text{total diss}}$ .

### 5.3.5 Ion Exchange Model

Ion exchange sorption is defined as the process by which a dissolved ion  $M_2$  is exchanged for an ion  $M_1$  that already occupies a surface sorption site and ion  $M_1$  is in turn released back into solution. The ion exchange reaction can be expressed as



where  $M_1$  = the ion initially occupying the exchange site,  
 $M_2$  = the ion replacing  $M_1$  on the exchange site;  
 $\text{SOH}\cdot\text{M}_1$  = surface sites occupied by ion  $M_1$   
 $\text{SOH}\cdot\text{M}_2$  = surface sites occupied by ion  $M_2$ , and  
 $a$  and  $b$  = stoichiometric coefficients.

The equilibrium constant (selectivity coefficient),  $K_{\text{ex}}$ , for the exchange reaction expressed as

$$K_{\text{ex}} = \frac{\{M_1\}^a \{\text{SOH}\cdot\text{M}_2\}^b}{\{M_2\}^b \{\text{SOH}\cdot\text{M}_1\}^a} = \frac{\gamma_{M_1}^a [M_1]^a [\text{SOH}\cdot\text{M}_2]^b}{\gamma_{M_2}^b [M_2]^b [\text{SOH}\cdot\text{M}_1]^a} . \quad (5.34)$$

The constant  $K_{\text{ex}}$  can be written in terms of concentrations by replacing activity of each species with the product of concentration and activity coefficient. The activity coefficients for the occupied sites,  $\text{SOH}\cdot\text{M}_n$ , are set equal to one as was assumed for the previous adsorption models in MINTEQA2.

### 5.3.6 Diffuse Layer Model

For the diffuse-layer model, the total charge,  $T_{\sigma_o}$ , for plane  $o$  is calculated as

$$T_{\sigma_o} = 0.1174 I^{1/2} \sinh(Z\psi_o F/2RT) \quad (5.35)$$

where  $Z$  = valency of the symmetrical electrolyte (which we take as unity),  
 $I$  = ionic strength, and

all other parameters are defined as in Equation 5.13.

Examples of surface reactions are listed below for protonation and deprotonation reactions as well as for a divalent cation  $M^{2+}$ . Boltzmann factors are represented in the mass action as components.

The surface reaction and corresponding mass action expression for the protonation reaction are, respectively,



and

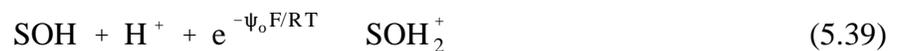
$$K = \frac{\{\text{SOH}_2^+\}}{\{\text{SOH}\} \{\text{H}_s^+\}} \quad (5.37)$$

where  $\text{H}_s^+$  denotes a hydronium ion near the surface.

The activity coefficients for the surface species  $\text{SOH}_2^+$  and  $\text{SOH}$  are assumed to be equal to unity. The activity of  $\text{H}_s^+$  must be corrected for the energy change required to move from the bulk solution to the charged surface. This activity change is represented by expressing  $\{\text{H}_s^+\}$  in terms of the activity of the bulk solution hydronium ion  $\{\text{H}^+\}$  and associated exponential Boltzmann expression for a charge  $z$  of 1 as

$$\{\text{H}_s^+\} = \{\text{H}^+\} e^{-\psi_0 F/RT} \quad (5.38)$$

Substituting this expression for  $\{\text{H}_s^+\}$  in Equations 5.36 and 5.37, one obtains the following surface reaction and mass action equation expressed in terms of the Boltzmann factor



and

$$K = \frac{\{\text{SOH}_2^+\}}{\{\text{SOH}\} \{\text{H}^+\} [e^{-\psi_0 F/RT}]} \quad (5.40)$$

The stoichiometry for the corresponding de-protonation reaction is



Substituting for  $\{\text{H}_s^+\}$  as above results in the following de-protonation surface reaction and mass action equation



and

$$K = \frac{\{SO^-\} \{H^+\} [e^{-\psi_o F/RT}]}{\{SOH\}} . \quad (5.43)$$

The stoichiometry for a surface reaction involving a multivalent species, such as a divalent cation  $M^{2+}$ , is



The mass action expression for this type of adsorption reaction also includes the charge and stoichiometry for the adsorbing ion. Substituting for  $\{M_s^{2+}\}$  and for  $\{H_s^+\}$  in Equation 5.44, one obtains the following mass action expressions

$$K = \frac{\{SO \cdot M^+\} \{H_s^+\}}{\{SOH\} \{M_s^{2+}\}} = \frac{\{SO \cdot M^+\} \{H^+\} [e^{-\psi_o F/RT}]}{\{SOH\} \{M^{2+}\} [e^{-\psi_o F/RT}]^2} \quad (5.45)$$

$$K = \frac{\{SO \cdot M^+\} \{H^+\}}{\{SOH\} \{M^{2+}\} [e^{-\psi_o F/RT}]} \quad (5.46)$$

Mass action expressions for other surface reactions are formulated in a similar manner.

### 5.3.7 Constant Capacitance Model

The constant capacitance model is a special case of the diffuse layer model, applicable in theory only to systems at high, constant ionic strength. The constant capacitance model is similar to the diffuse layer model in that they both define specific adsorption of all ions on the  $o$  plane. Except for the values of the equilibrium constants, the mass action and charge balance equations are identical for these 2 adsorption models. Therefore, the surface reactions and mass action expressions described above for the diffuse layer model also apply to the constant capacitance model.

The difference in these 2 models is in the function relating total surface charge,  $T_{\sigma_o}$ , to surface potential  $\psi_o$ . In the constant capacitance model, Equation 5.35 is approximated by

$$T_{\sigma_o} \approx C \psi_o \quad (5.47)$$

where  $C$  is a constant capacitance term. Although the constant capacitance and diffuse layer models are implemented similarly, the capacitance term  $C$  is often treated as a fitting parameter rather than as a measured characteristic of the system.

### 5.3.8 Triple Layer Model

The triple layer model (Figure 5.4) includes 2 adsorbing planes instead of 1 plane as conceptualized in the diffuse layer and constant capacitances models. As implemented in MINTEQA2, the *o* plane, the inner most zone, only includes the protonation and deprotonation (*i.e.*, gain or loss of H<sup>+</sup>) reactions at the surface sites. The  $\beta$  plane includes other specifically adsorbed ions with charge  $\sigma_\beta$  and potential  $\psi_\beta$  in that zone. The diffuse layer or '*d*' plane, which is the outer most zone, includes non-specifically adsorbed ions affected by  $\psi_d$  potentials. The capacitances between the *o* and  $\beta$  planes and the  $\beta$  and *d* planes are designated  $C_1$  and  $C_2$ , respectively. The user must provide values for both capacitance terms.

The total charges,  $T_{\sigma_o}$ ,  $T_{\sigma_\beta}$ , and  $T_{\sigma_d}$ , associated with *o*,  $\beta$ , and *d* planes, respectively, in the triple-layer model are defined as

$$T_{\sigma_o} = C_1(\psi_o - \psi_\beta) \quad (5.48)$$

$$T_{\sigma_\beta} = C_1(\psi_\beta - \psi_o) + C_2(\psi_\beta - \psi_d) \quad (5.49)$$

$$T_{\sigma_d} = C_2(\psi_d - \psi_\beta) \quad (5.50)$$

where  $\psi_o$  = electrostatic potential at the *o* plane,  
 $\psi_\beta$  = electrostatic potential at the  $\beta$  plane, and  
 $\psi_d$  = electrostatic potential at the *d* plane.

Surface reactions as expressed in the triple layer model differ from those used for the diffuse layer and constant capacitance models only in that their mass action expressions include the proper stoichiometry for the electrostatic components representing the  $\beta$  and *o* planes. The *d* plane, which has no specific adsorption, is therefore not a factor in the stoichiometry.

The surface protonation and deprotonation reactions for the triple layer model, except for their associated equilibrium constant values, are identical to those given above for the diffuse layer models. Examples of surface reactions and mass action expressions for the adsorption of a mono- and divalent cations and a monovalent anion adapted from Allison *et al.* (1991) are given below for the triple layer model. They show the stoichiometric coefficients for the electrostatic components representing the  $\beta$  and *o* planes.

The surface reaction for the adsorption of the monovalent metal cation M<sup>+</sup> is



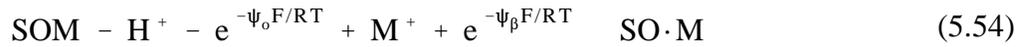
In the triple layer model,  $H_s^+$  and  $M_s^+$  occur in the  $\alpha$  and  $\beta$  planes, respectively. Therefore,

$$\{H_s^+\} = \{H^+\} [e^{-\psi_\alpha F/RT}] \quad (5.52)$$

and

$$\{M_s^+\} = \{M^+\} [e^{-\psi_\beta F/RT}] . \quad (5.53)$$

Substituting these expressions into Equation 5.51, the following MINTEQA2 reaction and mass action expression are obtained



and

$$K = \frac{\{SO \cdot M\} \{H^+\} [e^{-\psi_\alpha F/RT}]}{\{SOH\} \{M^+\} [e^{-\psi_\beta F/RT}]} . \quad (5.55)$$

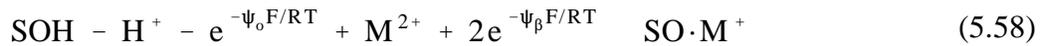
The surface reaction for the adsorption of the divalent metal cation  $M^{2+}$  is



For the divalent cation adsorbed in the  $\beta$  plane,

$$\{M_s^{2+}\} = \{M^{2+}\} [e^{-\psi_\beta F/RT}]^2 \quad (5.57)$$

Substituting this expression in the reaction above gives the following MINTEQA2 reaction and mass action expression



and

$$K = \frac{\{SO \cdot M^+\} \{H^+\} [e^{-\psi_\alpha F/RT}]}{\{SOH\} \{M^{2+}\} [e^{-\psi_\beta F/RT}]^2} . \quad (5.59)$$

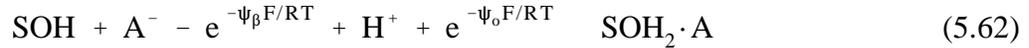
The surface reaction for the adsorption of the monovalent anion  $A^-$  is



This reaction results in the formation of a neutral surface complex. For the anion adsorbed in the  $\beta$  plane

$$\{A_s^-\} = \{A^-\} [e^{-\psi_\beta F/RT}]^- . \quad (5.61)$$

Substituting this into the above anion adsorption reaction, one obtains the following MINTEQA2 reaction and mass action expression



and

$$K = \frac{\{\text{SOH}_2 \cdot A\} [e^{-\psi_\beta F/RT}]}{\{\text{SOH}\} \{A^-\} \{H^+\} [e^{-\psi_o F/RT}]} . \quad (5.63)$$

The formulation of reactions and mass action expressions for other adsorbing cations and anions is similar to those examples given above.

## 5.4 Summary

Chemical reaction models are valuable computational tools that may be used to analyze the macro-chemical processes (*e.g.*, aqueous complexation, redox, solubility, and adsorption equilibrium) affecting the composition of a soil-water system being studied in the laboratory, field lysimeter, or field site. They also be used to provide some bounding calculations for predicting the changes in chemistry that will result when 1 or more of these processes are imposed on a soil-water system.

Numerous chemical reaction models exist. The MINTEQA2 computer code was developed with EPA funding and is currently distributed by EPA in a form that executes on personal computers. MINTEQA2 includes aqueous speciation, solubility (*i.e.*, saturation indices), precipitation/dissolution, and adsorption submodels. MINTEQA2's adsorption submodel includes 4 non-electrostatic [activity partition coefficient ( $K_d^{\text{act}}$ ), activity Langmuir, activity Freundlich, and ion exchange] models and 3 electrostatic (diffuse layer, constant capacitance, and triple layer) adsorption model options.

MINTEQA2 and other similar chemical reaction models can be used in indirect ways to support evaluations of  $K_d$  values and related contaminant migration and risk assessment modeling. These applications include the following:

- Calculation of aqueous speciation to determine the ionic state and composition of the dominant species for a dissolved contaminant present in a soil-water system
- Calculation of bounding, technically-defensible maximum concentration limits for contaminants (based on solubility constraints) as a function of key composition parameters (*e.g.*, pH) of any specific soil-water system

- Analysis of data from laboratory measurements of  $K_d$  values to determine if any solubility limits were exceeded during the experiments.

Chemical reaction models, however, cannot be used to predict a  $K_d$  value. The user must supply the adsorption parameters when using any of the adsorption model options. However, MINTEQA2 may be used to predict the chemical changes that result in the aqueous phase from adsorption using any of 7 adsorption model options.

The MINTEQA2 model includes an extensive thermodynamic database that is integrated with the aqueous speciation, solubility, and precipitation/dissolution submodels. Of the elements included in the project scope, the thermodynamic database distributed by EPA with MINTEQA2 does not contain reactions and associated thermodynamic data for aqueous species and solids containing cesium, plutonium, radon, and thorium. Published compilations of thermodynamic data for aqueous species, solids, and gases containing these elements are available that can be used as starting points for upgrading the MINTEQA2 database to include cesium, plutonium, radon, and thorium aqueous species and solids. MINTEQA2 does not have per se an integrated adsorption submodel database. The adsorption reactions and associated model parameters must be supplied by the user as part of each input file.